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| <p>(54) Title: SUBSTITUTED POLY(PHENYLENEVINYLENE)S AND POLY(NAPHTHALENEVINYLENE)S</p> <p>(57) Abstract</p> <p>The present invention relates to a novel class of electroluminescent ("EL") homopolymers, random co-polymers, and block co-polymers that includes repeating units of substituted (<i>para</i>-phenylenevinylene) ("PV") and/or substituted (1,4-naphthalenevinylene) ("NV") and methods for making the same. In general, the inventive homopolymers and copolymers are synthesized <i>via</i> ring opening polymerization ("ROMP") reactions by contacting a metathesis initiator with a corresponding substituted benzobarrelene or substituted barrelene. Novel methods for synthesizing substituted benzobarrelenes and barrelenes are also described.</p> | | |

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SUBSTITUTED POLY(PHENYLENEVINYLENE)S AND POLY(NAPHTHALENEVINYLENE)S

Inventors: Robert H. Grubbs and Michael W. Wagaman

5 This application claims the benefit of U.S. Provisional Application
No. 60/043,720 filed on April 17, 1997 entitled "Substituted
Poly(phenylenevinylene)s Soluble In Water And Organic Solvents" by
inventors Robert H. Grubbs and Michael W. Wagaman and which is
incorporated herein by reference.

10 The U.S. Government has certain rights in this invention pursuant to Grant
No. N00014-95-1-1319 awarded by the Navy, and Grant No. F49620-92-J-
0483 awarded by the Air Force.

BACKGROUND

15 The present invention generally relates to electroluminescent polymers and
methods for making the same. More particularly, the present invention
relates to a novel class of electroluminescent ("EL") polymers that includes
repeating units of substituted (*para*-phenylenevinylene) ("PV") and/or
substituted (1,4-naphthalenevinylene) ("NV").

20 Since the initial discovery in 1991 that poly-PV ("PPV") and other
conjugated polymers could be used as the emissive layer in light emitting
diodes ("LED"), an enormous amount of effort has been directed to
characterizing the physical and chemical properties of PPV and other
electroluminescent polymers. As the recent report of the use of 2-ethylhexyl-
5-methoxy phenylenevinylene ("MEH-PPV") in organic polymer lasers
demonstrates, these polymers are no longer merely of theoretical interest and
25 are now being used in practical applications.

5 The overwhelming interest in organic emissive layers has been motivated in part by the potential diversity and functionality that are possible from organic chemistry. Although small organic molecules were originally targeted, light emitting layers must be made by vapor deposition of these materials to create the uniform, thin layers that emit light efficiently. In contrast to the cost and difficulty of vapor deposition, spin casting methods may be used to make light emitting layers from soluble EL polymers.

10 Although several EL polymers, particularly MEH-PPV, are now commonly used, molecular calculations suggest that their properties could be improved by adding certain functional groups to at least some of the polymer's repeating units. For example, a disadvantage to MEH-PPV devices is that it must be rigorously encapsulated since the MEH-PPV emitting layer tends to oxidize in the presence of air. Because this air instability is due to the electron donating effect of the alkoxy groups, PPVs that are substituted with one or more electron withdrawing groups are believed to have improved air stability. In addition, due to the effect of the electron withdrawing groups on the position of molecular orbitals, these substituted PPVs are also believed to have better light emitting characteristics as well.

20 Another potential improvement or modification is EL polymers with blue emission for making full colored LED displays. Because full colored LED displays require materials that emit the three primary colors of light (blue, green and red), this technology has been stalled because of the lack of suitable blue emitters.

25 In addition, molecular orbital calculations have suggested that block copolymers would have improved luminescence efficiencies relative to homopolymers. These simulations indicate that when a conjugated block

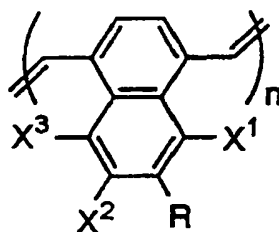
copolymer is made up of two polymers with different bandgaps, the electron-hole pairs ("excitons") formed in the larger bandgap block will migrate to the smaller bandgap block so that the copolymer exhibits the luminescence characteristic of only the smaller bandgap material. Because excitons that originated in blocks of either type of polymer recombine in the smaller bandgap material and are not free to migrate through the entire length of the polymer, the luminescence intensity of this material will be greater than that of a homopolymer of the same material.

Despite the enormous potential, the diversity of EL polymers have yet to be fully explored because the known synthetic routes to PPV and PNV are not readily amenable to forming substituted PPVs and PNVs. As a result, a need exists for novel synthetic routes for making substituted PVs and NVs and incorporating these monomers into novel EL homopolymers and copolymers.

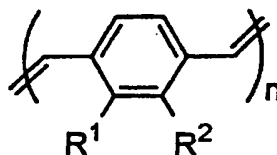
SUMMARY

The present invention relates to a novel class of electroluminescent ("EL") polymers that includes repeating units of substituted (*para*-phenylenevinylene) ("PV") and/or substituted (1,4-naphthalenevinylene) ("NV") and methods for making the same.

In one aspect of the invention, novel homopolymers, random copolymers, and block copolymers are described which include at least one repeating unit of either substituted PV or substituted NV having the formula:

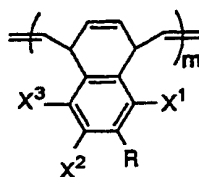


or

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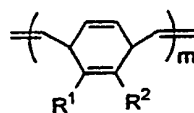
wherein n is a positive integer; X^1 , X^2 , X^3 are each either hydrogen or any electron withdrawing group; R , R^1 and R^2 are each hydrogen, halide, or a substituted or unsubstituted moiety selected from a group consisting of C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, and aryl, the moiety optionally functionalized with one or more functional groups selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, peroxy, anhydride, carbamate, and halogen. The moiety substitution is selected from a group consisting of C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, and aryl, each of which also may be optionally functionalized with one or more functional groups selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, peroxy, anhydride, carbamate, and halogen.

The inventive homopolymers, random copolymers, and block copolymers may additionally include one or both repeating units of the formula:



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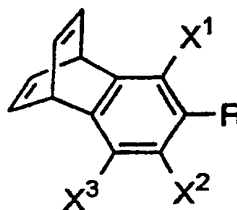
or



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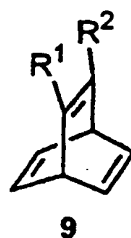
wherein m is an integer and X^1 , X^2 , X^3 , R , R^1 , and R^2 are as previously defined.

In another aspect of the invention, methods for synthesizing the above described polymers are described. These methods are generally ring opening polymerization reactions ("ROMP") which comprise contacting a metathesis catalyst initiator with a substituted benzobarrelene having the formula



3

or with a substituted barrelene having the formula



wherein X^1 , X^2 , X^3 , R , R^1 , and R^2 are as previously defined.

In yet another aspect of the invention, methods for synthesizing substituted benzobarrelenes and substituted barrelenes, the necessary monomers for making the inventive polymers are also described.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 displays the photoluminescence of 100% aromatized di-*t*-butyl ester PPV and an 80% aromatized di-*t*-butyl ester PPV.

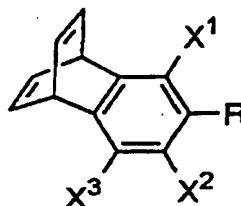
Figure 2A shows the emission intensities of bistrifluoromethyl PPV homopolymer, octyltrichloro PNV homopolymer, bistrifluoromethyl PPV/octyltrichloro PNV block copolymer and bistrifluoromethyl PPV/octyltrichloro PNV random copolymer when irradiated at the excitation maximum of bistrifluoromethyl PPV (345 nm).

Figure 2B shows the emission intensities of octyltrichloro PNV homopolymer, bistrifluoromethyl PPV/octyltrichloro PNV block copolymer and bistrifluoromethyl PPV/octyltrichloro PNV random copolymer when irradiated at the excitation maximum of octyltrichloro PNV (430 nm).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

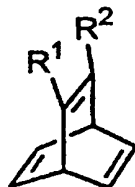
The present invention relates to a novel class of electroluminescent ("EL") polymers that includes repeating units of substituted (*para*-phenylenevinylene) ("PV") and/or substituted (1,4-naphthalenevinylene) ("NV") and methods for making the same. Practice of the present invention allows the synthesis of a diverse set of novel EL polymers with improved luminescent characteristics and added functionalities.

The first step in making novel EL polymers is the synthesis of the requisite substituted monomers. Although a variety of monomers may be used to make EL polymers, the two preferred monomers in the practice of the present invention are substituted benzobarrelenes having the formula:



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and substituted barrelenes having the formula

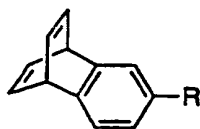


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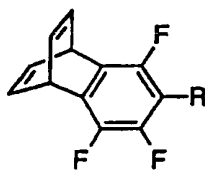
wherein X^1 , X^2 , X^3 are each hydrogen or any electron withdrawing group; R, R^1 and R^2 are each hydrogen, halide, or a substituted or unsubstituted moiety selected from a group consisting of C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, and aryl, the moiety optionally functionalized with one or more

functional groups selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, peroxy, anhydride, carbamate, and halogen. The moiety substitution is selected from a group consisting of C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, and aryl, each of which may also be optionally functionalized with one or more functional groups selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, peroxy, anhydride, carbamate, and halogen. In addition, R^1 and R^2 may together form a cyclic moiety.

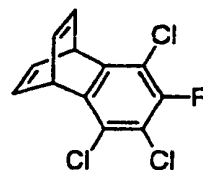
Substituted benzobarrelenes wherein $X^1 = X^2 = X^3$ and are all either hydrogen or halide are particularly preferred. In the most preferred embodiments, X^1 , X^2 , and X^3 are all selected from the group consisting of hydrogen, fluoride, and chloride and R is C_1 - C_{10} alkyl. Illustrative examples of the most preferred embodiments of substituted benzobarrelenes are:



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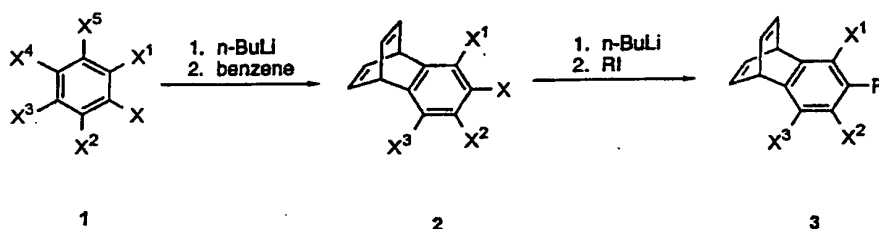
wherein R is a C_1 - C_{10} alkyl.

Similarly, substituted barrelenes in which R^1 and R^2 are each an electron withdrawing group is particularly preferred. Illustrative examples of suitable

electron withdrawing group includes but are not limited to C₁-C₂₀ perfluoroalkyl, C₁-C₂₀ carboxylic acid, C₁-C₂₀ carboxylate, C₁-C₂₀ ester, C₁-C₂₀ acid halide, C₂-C₂₀ acid anhydride, and C₁-C₂₀ amide. In most preferred embodiments, R¹ and R² are each selected from the group consisting of hydrogen, C₁-C₁₀ perfluoroalkyls, and C₁-C₁₀ esters.

The substituted benzobarrelenes and barrelenes may be made by any conventional methods known in the art. However, because some of the preferred substituted benzobarrelenes and barrelenes could not be synthesized using previously described methods, novel synthetic protocols were developed.

Because requisite substituted monomers are necessary to the practice of the present invention, one aspect of the invention involves novel protocols for making particular substituted benzobarrelenes and barrelenes. As illustrated by Scheme 1, one embodiment of the inventive protocols is for the synthesis of a particularly useful class of alkyltrihalobenzobarrelenes.

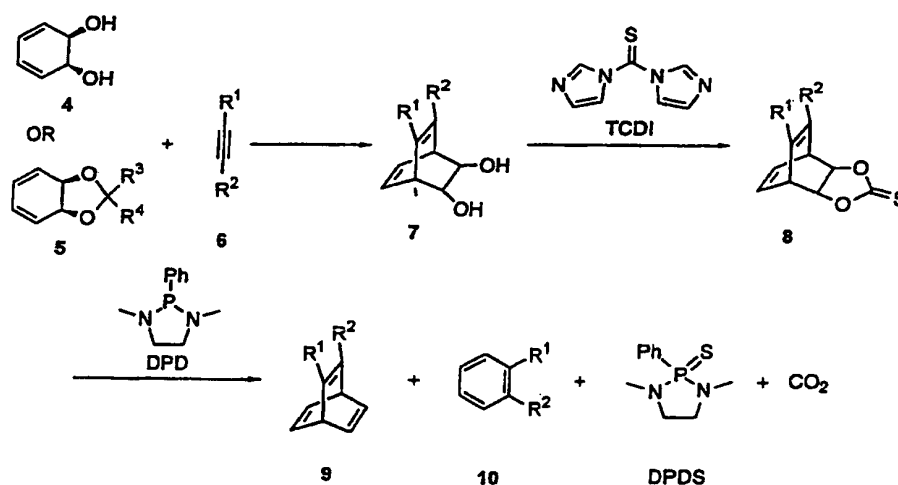


If an alkylated trifluorobenzene is desired, the substituted benzene 1 is 1-bromo-4-chloro-2,3,5,6-tetrafluorobenzene and is reacted with n-butyl lithium ("n-BuLi") to yield chlorotrifluorobenzobarrelene 2 (wherein X = Cl)

and $X^1 = X^2 = X^3 = F$). Compound 2 is further reacted with *n*-BuLi and alkyl iodide ("RI") to yield alkyltrifluorobenzobarrelene 3. If an alkylated trichlorobenzobarrelene is desired, substituted benzene 1 is hexachlorobenzene and is reacted with *n*-BuLi to yield tetrachlorobenzobarrelene 2 (wherein $X = X^1 = X^2 = X^3 = Cl$). Compound 2 is further reacted with *n*-BuLi and alkyl iodide ("RI") to yield alkyltrichlorobenzobarrelene 3. Both alkyltrichlorobenzobarrelene and alkyltrifluorobenzobarrelene may be dehalogenated using Na and *t*-butyl alcohol to yield the corresponding alkylbenzobarrelene (compound 3 wherein $X^1 = X^2 = X^3 = H$).

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Scheme 2 illustrates another embodiment of the inventive protocols.



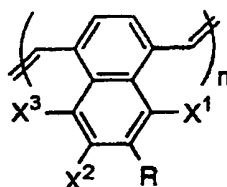
In contrast to previously known mutually exclusive methods for making unsubstituted barrelene and substituted barrelenes, the inventive protocol may be used to make both unsubstituted barrelene and substituted barrelenes. Typically, either *cis*-3,5-cyclohexadiene-1,2-diol 4 or the acetonide protected

form of this molecule 5 is reacted with $R^1C\equiv CR^2$ 6 in a Diels-Alder reaction to yield the barrelene diol 7. If compound 5 is used instead of compound 4, reaction with 6 yields an acetal form of compound 7. The acetal is deprotected under acidic conditions to yield compound 7. Compound 7 is converted to thiocarbonate 8 using thiocarbonyldiimidazole ("TCDI"). Substituted barrelene 9 is obtained by reacting thiocarbonate 8 with 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine ("DPD").

Because the acetonide protected form of *cis*-3,5-cyclohexadiene-1,2-diol 5 typically results in a near quantitative yield of the Diels-Alder adduct, the use of compound 5 is generally preferred over that of the unprotected diol 4. Although R^3 and R^4 of compound 5 may be any suitable group, embodiments of compound 5 wherein $R^3 = R^4 = \text{methyl}$ and $R^3 = \text{H}$ and $R^4 = \text{phenyl}$ are especially preferred.

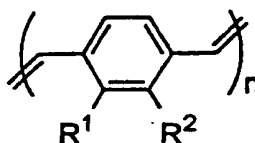
If only a monosubstituted barrelene is desired, a substituted alkynyl *p*-toluenesulfate ($\text{TsC}\equiv\text{CR}$) is used instead of compound 6. The *p*-toluenesulfone group is removed by reductive desulfonylation and the diol is deprotected under acidic conditions. However, because the use of HCl could result in decomposition, the use of methanol and pyridinium to deprotect the diol is generally preferred in this synthesis.

Another aspect of the present invention relates to novel EL polymers which include at least one repeating unit of either substituted PV or substituted NV having the formula



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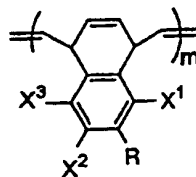
or substituted PV having the formula



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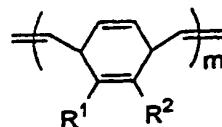
wherein n is a positive integer, and X^1 , X^2 , X^3 , R , R^1 , and R^2 are as previously defined. Polymers which include substituted NVs wherein $X^1 = X^2 = X^3$ and are all either hydrogen or halide are particularly preferred. In the most preferred polymer embodiments, X^1 , X^2 , and X^3 are all selected from the group consisting of hydrogen, fluoride, and chloride and R is C_1 - C_{10} alkyl. Similarly, polymers which include substituted PVs in which R^1 and R^2 are each an electron withdrawing group is particularly preferred. Illustrative examples of suitable electron withdrawing group includes but are not limited to C_1 - C_{20} perfluoroalkyl, C_1 - C_{20} carboxylic acid, C_1 - C_{20} carboxylate, C_1 - C_{20} ester, C_1 - C_{20} acid halide, C_2 - C_{20} acid anhydride, and C_1 - C_{20} amide. In most preferred embodiments, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1 - C_{10} perfluoroalkyls, and C_1 - C_{10} esters.

In another polymer embodiment, the EL polymers include at least one repeating unit of an unaromatized precursor of substituted NV having the formula



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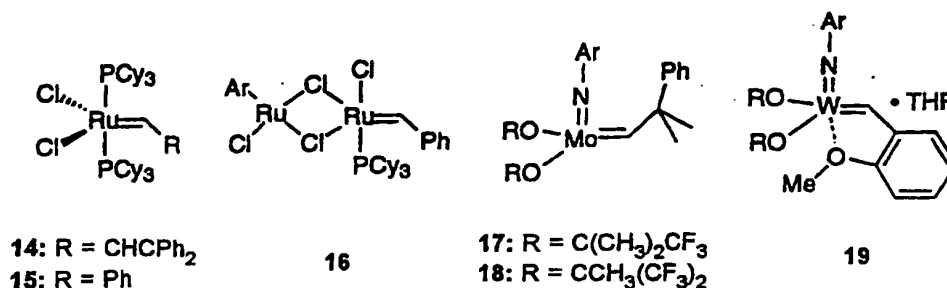
or an unaromatized precursor of substituted PV having the formula



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5 wherein m is a positive integer, and X^1 , X^2 , X^3 , R , R^1 , and R^2 are as previously defined.

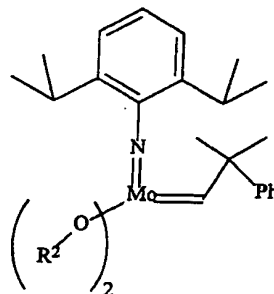
10 The substituted NVs and PVs and their respective unaromatized precursors may be incorporated into polymers as homopolymers, block copolymers, or random copolymers via ring opening polymerization reactions ("ROMP") of the corresponding substituted benzobarrelene or barrelene with a metathesis catalyst or initiator. Illustrative examples of metathesis initiators include but are not limited to the following:



However, because solubility of the inventive polymers is improved when some *cis*-olefins are interspersed in the polymer backbone (over an all *trans* polymer backbone), metathesis initiators that also form *cis*-bonds are generally preferred. For example, polymers formed from ROMP of substituted benzobarrelene and/or substituted barrelene using compound 18 (which forms interspersed *cis*-bonds) generally resulted in polymers that were soluble at room temperature in common organic solvents (*i.e.* chloroform, dichloromethane, chlorobenzene, and *cis*-dichlorobenzene). Moreover, because it is desirable to use the catalyst to make both homopolymer and block co-polymers, catalysts which result in living polymerization are generally preferred. As a result, metathesis catalyst which forms some *cis*-bonds as well as result in living polymerization are especially preferred.

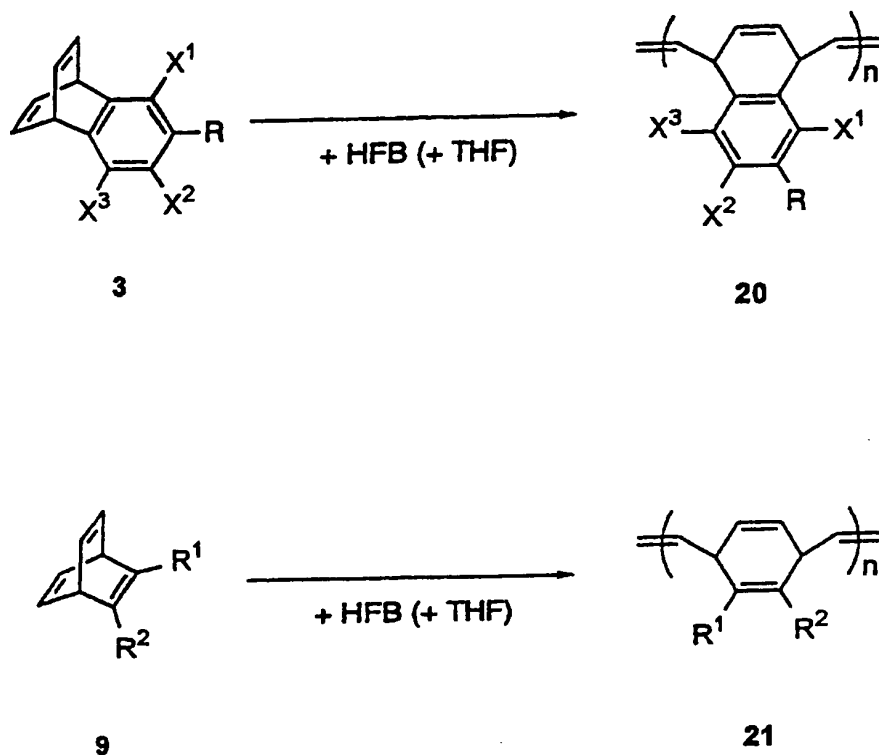
If desired, activators may also be added to the catalyst composition to enhance the rate of catalyst initiation. An illustrative example of such an initiator is hexafluoro-*t*-butanol. In addition, to further maximize initiation, a modulator that slows the rate of propagation may also be included. Suitable examples of catalyst modulators are Lewis bases which reduce metathesis activity by reversibly coordinating to the metal center. Illustrative examples of catalyst modulators are phosphines, phosphites and tetrahydrofuran ("THF").

The most preferred catalyst for the practice of the present invention is compound 18 (henceforth also referred to as the "Mo metathesis initiator"):

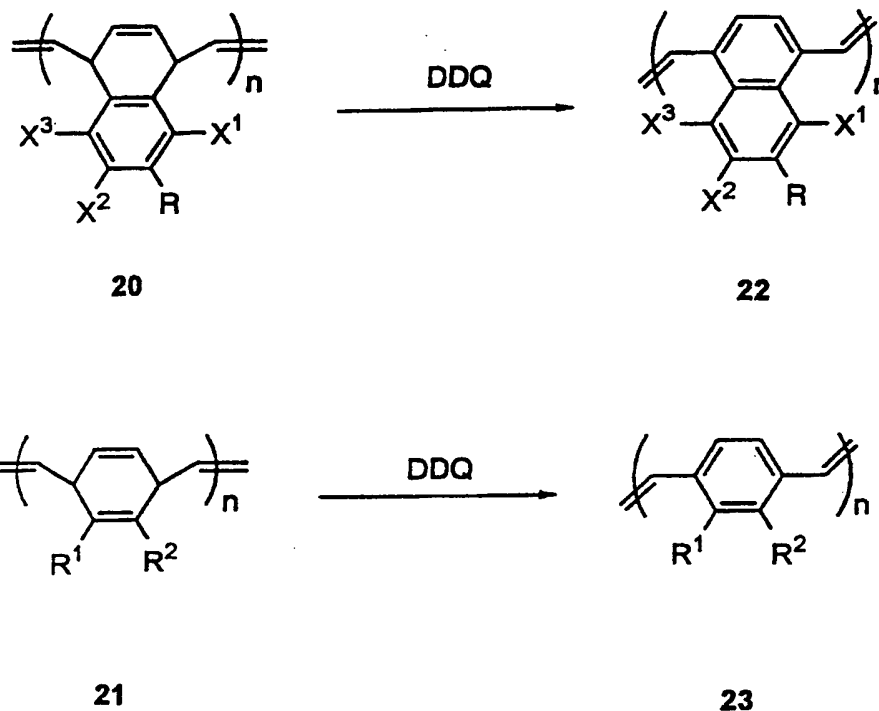


wherein R² is -C(CH₃)(CF₃)₂.

5 The inventive polymers are generally synthesized *via* ROMP reactions of the corresponding monomers with the Mo metathesis initiator in the presence of HFB and THF. The general protocol is illustrated by Scheme 3:



wherein n is a positive integer, and X^1 , X^2 , X^3 , R , R^1 , and R^2 are as previously defined. The unaromatized precursor polymer, **20** or **21**, is then aromatized. A suitable method for this purpose is reacting the precursor polymer with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone ("DDQ"). The aromatization reaction is shown by Scheme 4.

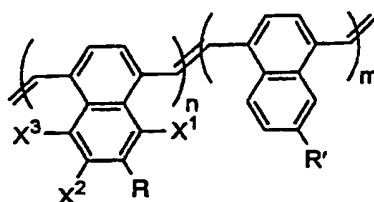


Because partially aromatized polymers are both more soluble and show a higher quantum yield than their fully conjugated counterparts, they are generally preferred. An illustration of this phenomenon is shown by Figure 1 which displays the photoluminescence of 100% aromatized di-*t*-butyl ester PPV and an 80% aromatized di-*t*-butyl ester PPV.

Using the above described protocol, the inventive homopolymers are formed when only one monomer is used during the polymerization reaction. Similarly, random copolymers are made by mixing at least two monomers together prior to the polymerization reaction. However, to make well-defined block copolymers, sequential polymerization of the individual monomers is

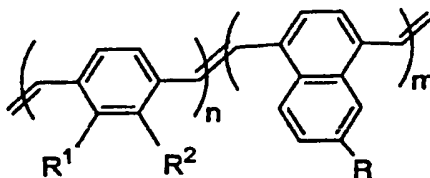
required. As further explained in the Examples and in the Experimental Methods sections, the next monomer typically is not added until all the previous monomer is fully consumed (as measured by ^1H NMR). Any number of monomers may be polymerized in succession to form block polymers. However, copolymers made from two monomers wherein one material has a smaller bandgap than the other is generally preferred.

Illustrative examples of block copolymers include:



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and



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wherein m and n are positive integers; R' is defined similarly to R; and X¹, X², X³, R, R¹, and R² are as previously defined.

EXAMPLE 1

Attempts to Synthesize Alkylated Trihalobenzobarrelene Using Variation of Traditional Routes

5 Alkylated trifluorobenzobarrelenes were desired so that the effect of the electron withdrawing fluorines on the band gap of PNV could be studied and compared to the unfluorinated counterparts. However, attempts to do so using a variation of Method A to prepare 6-undecyl-1,4-dihydro-1,4-ethanonaphthalene produced only very low yields of alkylated trifluorobenzobarrelenes. Method A is described in detail below in the
10 Experimental Methods Section.

Instead, the procedure had to be modified to resemble the protocol that is reported for the alkylation of bromonaphthalene by Merrill and Negishi in *J. Org. Chem.* 39: 3452 (1974) wherein the necessary alkylated benzenes were prepared by a modified procedure similar to that reported for the alkylation
15 of bromonaphthalene. In general, 1-bromo-4-chloro-2,3,5,6-tetrafluorobenzene was dissolved in dry THF and cooled to -78 °C in a dry ice/acetone bath. Butyl lithium in hexane was added followed by alkyl bromide forming 1-chloro-4-alkyl-tetrafluorobenzene.

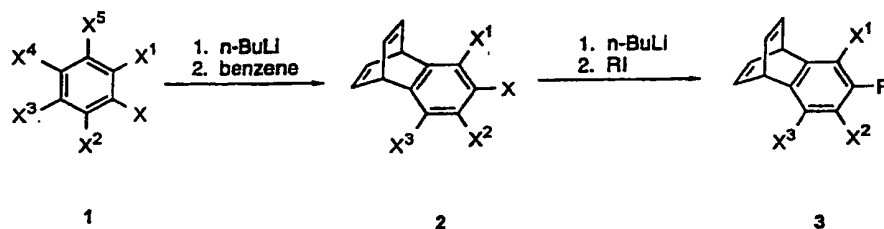
Purified 1-chloro-4-alkyl-tetrafluorobenzene was then dissolved in ether and combined with *cis*-1,2-benzylidenedioxy-3,5-cyclohexadiene which was also dissolved in ether. Butyl lithium was added to the reaction mixture to form
20 6-alkyl-5,7,8-trifluoro-1,2,3,4-tetrahydro-2,3-(benzylidenedioxy)-1,4-ethanonaphthalene. However, all attempts to convert this intermediate into 6-alkyl-5,7,8-trifluoro-1,4-dihydro-1,4-ethanonaphthalene by base catalyzed
25 fragmentation of the essentially failed with the best yield of the final product being less than 5%.

Diels-Alder reaction was carried out as reported by Hales *et al.*, *Org. Synth.* 59: 71 (1979) for the synthesis of tetrachlorobenzobarrelene (butyl lithium in benzene) in another attempt to avoid the acetal elimination step and shorten the overall synthesis. ^1H NMR indicated that the product yield was between 40-45%. However, because the products were not separable by column chromatography, purification was attempted by distillation. This resulted in isolation of some final product but retro Diels-Alder decomposition of the benzobarrelene reduced the yield of the isolated product to about 10%.

EXAMPLE 2

Novel Route to Alkylated Tri-Halobenzobarrelenes and Alkylated Benzobarrelenes

The general protocol for synthesizing tri-halobenzobarrelenes is as follows:



wherein X , X^1 , X^2 , X^3 , X^4 , and X^5 are each a halogen and R is alkyl. In preferred embodiments X is chloride and $\text{X}^1=\text{X}^2=\text{X}^3$ are either all chloride or fluoride. In especially preferred embodiments, compound 1 is either 1-bromo-4-chloro-2,3,5,6-tetrafluorobenzene which would result in an alkylated trifluorobenzobarrelene or hexachlorobenzene which would result in an alkylated trichlorobenzobarrelene.

Table 1 displays the yields for an illustrative set of alkyltrichlorobenzobarrelenes and alkyltrifluorobenzobarrelenes.

Table 1. Results of alkylation of **2** and **21**.

| | product | R | $X^1=X^2=X^3$ | % yield |
|----|---------|---------------------------------------|---------------|---------|
| 5 | 3a | $-(CH_2)_3CH_3$ | F | 88 |
| | 3b | $-(CH_2)_7CH_3$ | F | 91 |
| | 3c | $-(CH_2)_2CH(CH_3)_2$ | F | 83 |
| | 3d | $-(CH_2)_7CH_3$ | Cl | 78 |
| | 3e | $-(CH_2)_{10}CH_3$ | Cl | 92 |
| 10 | 3f | $-(CH_2)_2CH(CH_3)_2$ | Cl | 86 |
| | 3g | $-(CH_2)_2CH(CH_3)(CH_2)_3CH(CH_3)_2$ | Cl | 90 |
| | 3h | $-CH_2CH(CH_2CH_3)(CH_2)_3CH_3$ | Cl | 5 |

As shown by Table 1, only one alkyl iodide **3h** resulted in a low yield of the final product. Because this alkyl group was branched on the carbon alpha to the iodine substituted carbon, the low yield of the alkylated benzobarrelene is believed due to the competing elimination reaction.

In all cases, only a single alkylated product was observed. This is expected in the case of chlorotrifluorobenzobarrelenes since alkylation should only occur by displacement of chlorine. However, for tetrachlorobenzobarrelene, alkylation could conceivably occur by displacement of a chlorine in either the 3- or 4- position, or multiple alkylation could occur. Curiously, only products of displacement of the chlorine in the 4-position were observed.

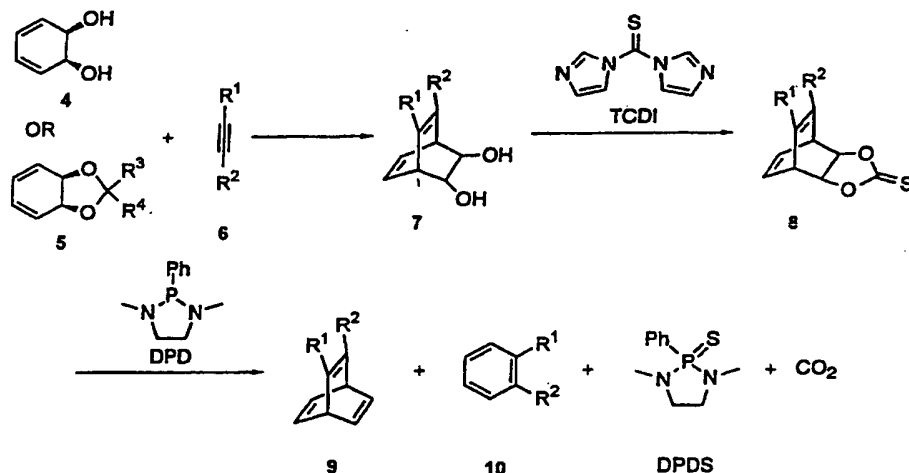
If desired, alkylated benzobarrelenes were obtained in high yields ($\approx 97\%$) by reacting the corresponding alkyltrihalobenzobarrene with Na and *t*-BuOH to

remove the halogens. In addition to providing a simple route to the alkylated benzobarrelenes, conversion to the unhalogenated benzobarrelene also offered confirmation of the substitution pattern of the synthetic route described by the above protocol. For example, the product obtained by dechlorination of undecyltrichlorobenzobarrelene ("5-undecyl-1,8-dihydro-1,8-etheno-3,4,6-trichloronaphthalene") were found to have a ^1H NMR spectrum identical to that observed for the undecylbenzobarrelene ("6-undecyl-1,4-dihydro-1,4-ethenonaphthalene") made as described by Method A in the Experimental Methods Section.

EXAMPLE 3

New Efficient Synthesis of Both Substituted and Unsubstituted Barrelenes (Bicyclo[2.2.2]octatrienes)

The general protocol for the synthesis of substituted barrelenes is as follows:



Either *cis*-3,5-cyclohexadiene-1,2-diol **4** or the acetonide protected form of this molecule **5** is reacted with $\text{R}^1\text{C}\equiv\text{CR}^2$ in a Diels-Alder reaction to yield the barrelene diol **7**. If compound **5** is used instead of compound **4**, reaction

with 6 yields an acetal form of compound 7. The acetal is deprotected under acidic conditions to yield compound 7. Compound 7 is converted to thiocarbonate 8 using thiocarbonyldiimidazole ("TCDI"). Substituted
5 barrelene 9 is obtained by reacting thiocarbonate 8 with 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine ("DPD").

Because the acetonide protected form of *cis*-3,5-cyclohexadiene-1,2-diol 5 typically yielded the Diels-Alder adduct in near quantitative yield, using it is generally preferred over the unprotected diol 4. Although R³ and R⁴ may be any suitable group, embodiments of compound 5 wherein R³ = R⁴ = methyl
10 and R³ = H and R⁴ = phenyl are especially preferred.

If only a monosubstituted barrelene is desired, the use of a substituted alkynyl *p*-toluenesulfate (TsC≡CR) is preferred. The *p*-toluenesulfone group is removed by reductive desulfonylation and the diol was deprotected under acidic conditions. However, because the use of HCl could result in
15 decomposition, the use of methanol and pyridinium to deprotect the diol is generally preferred.

EXAMPLE 4

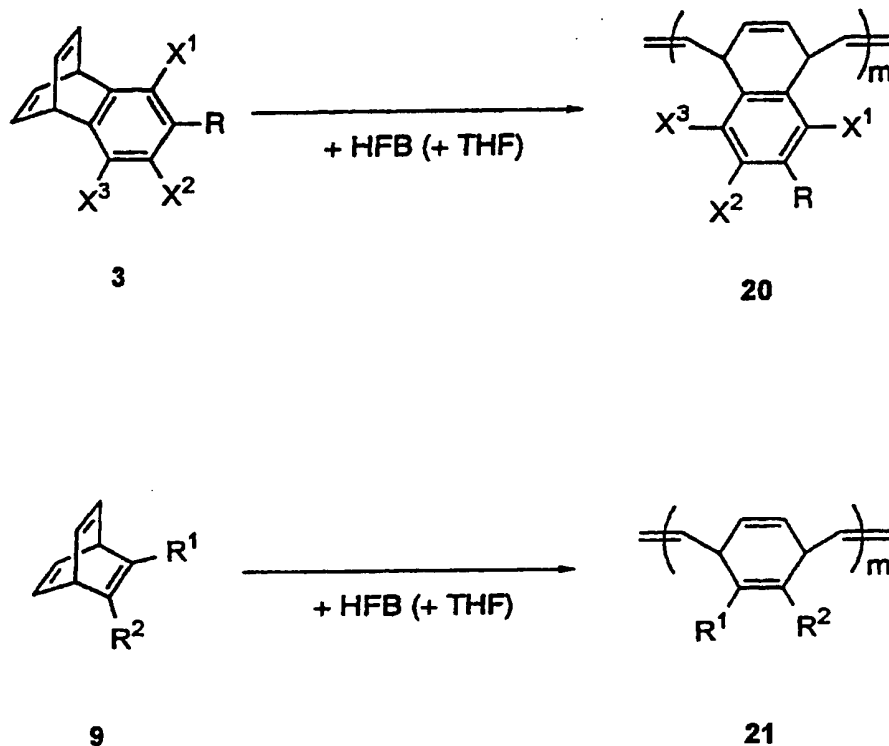
Living polymerization was achieved using Mo metathesis initiator by
20 activating the catalyst with hexafluoro-*t*-butanol ("HFB"). In general, the percentage of the catalyst that became initiated increased with increasing amounts of HFB. However, an upper limit is reached at about 50 equivalents of HFB at which point the catalysts begins to decompose. The best activity was observed when between about 14 and about 20 equivalents of HFB was
25 used.

In addition to achieving better initiation, the polymerization was much more rapid in the presence of HFB. For example, polymerization of undecylbenzobarrelene (or compound 11) in the presence of 14 equivalents of HFB takes about 35 minutes versus between about 10-18 hours when HFB is not added. To maximize initiation relative to propagation, the activity of the Mo metathesis initiator was further tuned with Lewis bases. Although any suitable Lewis base may be used to slow the rate of propagation, the use of tetrahydrofuran ("THF") is especially preferred. The best results were achieved when about 10 equivalents of THF was used during the polymerization reaction.

EXAMPLE 5

Polymerization

In general, polymers were formed via ring opening metathesis polymerization ("ROMP") reactions of either substituted benzobarrelenes or substituted barrelenes as illustrated by Scheme 3:



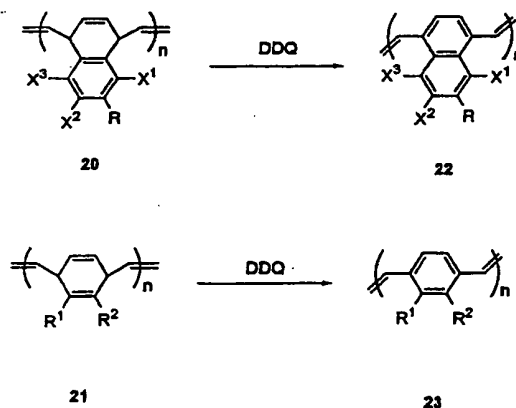
Inside a nitrogen filled dry box, the desired amount of monomer ($\approx 50 - 150$ mg depending on the monomer and the monomer to catalyst ratio desired) was dissolved in $0.5 - 0.6$ g of dry degassed benzene and the required amount of dry hexafluoro-*t*-butanol (usually ≈ 7.8 μ L) was added. Mo metathesis initiator ($3.5 - 3.9$ mg) dissolved in 10 drops of dry C_6D_6 was then added to this solution. The reaction mixture changed color from yellow to light orange or orange-brown during the first few minutes after mixing. For following the reaction by 1H NMR, the solution was transferred into an NMR tube equipped with a J-Young valve. After the polymerization was shown to be complete, if a block copolymer was being made, the NMR tube was returned to the dry box and the second monomer was added. After the

polymerization was complete, degassed benzaldehyde was added to quench the initiator. The reaction mixture, which turned brown over 30 minutes, was then pipetted into degassed methanol and the resulting precipitate was recovered by centrifuging and then decanting the solvent. Further purification was accomplished by redissolving the polymer in dichloromethane or benzene and then reprecipitating the polymer in methanol. The polymer was then dried under vacuum. GPC studies were conducted by dissolving a sample of this polymer in dichloromethane.

EXAMPLE 6

Polymer Aromatization

The desired amount of polymer was dissolved in methylene chloride, C_6D_5Br or hexafluorobenzene and DDQ, was added. Scheme 4 illustrates these reactions:



For fast reactions done in dichloromethane, DDQ was dissolved in dichloromethane before adding it to the polymer solution. In most cases slightly less (≈ 0.95 equiv.) than one equivalent of DDQ was added since polymers containing some unaromatized units were found to be significantly more soluble than the fully aromatized polymers. In a few cases, 1.5 - 2

equivalents of DDQ was required to reach the desired levels of aromatization. Reactions done in dichloromethane generally proceeded at room temperature. For reactions done in C_6D_5Br or hexafluorobenzene the reaction flask was sealed and heated in an oil bath at 120°C for 1 - 3 days. After this time, 1H NMR of the crude mixture showed <5% of the unaromatized polymer remaining. The reaction mixture was then added to methanol to yield a precipitate which was isolated by centrifuge and further purified by repeated precipitation as for the precursor polymers. To ensure that all of the polymer precipitated each time, the solvent layer above the precipitated polymer was spotted several times on a non-luminescent TLC plate. This plate was then irradiated with a hand-held UV lamp to see if any polymer, which is luminescent, had remained in solution. In some cases, adding a minimal amount (0.5 - 1 mL was added to the 40 - 50 mL of solvent mixture generated by the precipitation procedure) of methanol saturated with sodium chloride was found to facilitate precipitation.

EXAMPLE 7

Photoluminescence Measurements

Approximately 2 mg of each polymer was dissolved in 50 mL of chloroform to yield solutions of each polymer so that each solution A contained the same concentration of total monomer units. 1 mL of each of these solutions was then diluted to 25 mL using chloroform to yield solutions B. 1 mL of each of these solutions was then diluted to 25 mL using chloroform to yield solutions C. Solutions B and C were used for most luminescence measurements. However, solution A was sometimes used for those polymers that displayed weak luminescence.

All measurements were performed on solutions that were diluted so that the emission maximum was on scale with a $Ru(bpy)_3Cl_2$ standard that was

approximately 1×10^{-5} M. The exact concentration used in calculating quantum yields (7.6×10^{-6} M) was calculated from the absorbance of this solution at 453 nm and the reported extinction coefficients. All polymer solutions were prepared using degassed solvent. Quantum yields for the polymers were calculated by comparison to a $\text{Ru}(\text{bpy})_3\text{Cl}_2$ standard using the equation:

$$\Phi_{poly} = \frac{I_{poly} \cdot \epsilon_{Ru} C_{Ru}}{I_{Ru} \cdot \epsilon_{poly} C_{poly}} \cdot \Phi_{Ru}$$

Integration values, I , were measured on spectra that had been corrected for detector response using the software provided with the SLM 8000 C Spectrofluorometer. A value of 0.028 ± 0.002 was used for Φ_{Ru} . The $\text{Ru}(\text{bpy})_3\text{Cl}_2$ solution was equilibrated with air.

In the case of co-polymers, most measurements on films were also performed using the SLM 8000 C Spectrofluorometer. In this case, a film of the polymer was formed by putting a few drops of a concentrated solution of the polymer on a glass slide and allowing the solvent to evaporate. The slide was then cut to fit into the cuvette holder in the spectrofluorometer. This technique allowed collection of the emission spectrum, but did not provide quantitative data. Quantum yields for films of the polymers were measured as previously reported (*i.e.* Braun *et al.*, *Synth. Met.* 66: 75 (1994)).

EXAMPLE 8

The aromatized polymers were usually brightly colored and luminesced strongly under a hand held UV lamp. As shown in Table 2, the different

homopolymers exhibited luminescence at a range of wavelengths that cover the visible spectrum from blue (≈ 450) to nearly red (579 nm).

Table 2. Absorbance and photoluminescence data for the PNVs and PPVs.

| | Polymer ^a | Solvent | λ_{abs} soln. | λ_{em} soln. ^b | Φ soln. (%) ^g | λ_{em} film |
|----|--|-------------------------------|---------------------------------|--|----------------------------------|-------------------------------|
| 5 | undecyl PNV | CHCl ₃ | 444 | 551 ^c , 561 ^d | 0.5 | 593 |
| | octyltrifluoro PNV | CHCl ₃ | 416 | 568 ^c , 579 ^d | 0.05 | e |
| | octyltrichloro PNV | CHCl ₃ | 437 | 569 | 14 | 570 |
| | PPV | insoluble | 442 ^f | insoluble | 15 ^f | 558 |
| | dimethylester PPV | CHCl ₃ | 400 | 479 | 33 | e |
| 10 | di- <i>t</i> -butylester PPV | CHCl ₃ | 410 | 479 | 72 | 527 |
| | di- <i>t</i> -butylester PPV (80%) | CHCl ₃ | 408 | 479 | ≈ 100 | e |
| | bistrifluoromethyl PPV | CHCl ₃ | 308 | 449 | 20 | 458 |
| | trifluoromethyl perfluorooctyl PPV | C ₆ F ₆ | 328 | 443 | 65 ^h | 465 |
| 15 | di- <i>t</i> -butyl carboxylate PPV | 0.1 N NaOH (aq) | 424 | 491 | 16 | e |

a) Samples were at least 95% aromatized except as noted in parentheses. b) Excitation wavelengths are as listed in the Experimental section. c) Value obtained by excitation at 403 nm, which is the excitation maximum of octyltrifluoro PNV. d) Value obtained by excitation at 485 nm, which is the excitation maximum of undecyl PNV. e) Data was not obtained for films of these materials. f) Since PPV is insoluble, the absorbance maximum and quantum yield for films of this material is listed. g) Quantum yield values were calculated by comparison to Ru(bpy)₃Cl₂. h) This quantum yield is higher than that of bistrifluoromethyl PPV due to the different solvent used.

25 As predicted, the emission of PNVs substituted with electron withdrawing groups (fluoride and chloride) exhibited a red shift relative to the unhalogenated PNV. Both the absorbance and emission maxima of the substituted PPVs were also strongly blue shifted relative to films of unsubstituted PPV.

When the polymers were tested at 80% and 100% aromatization, the partially aromatized polymer showed a higher quantum yield than the fully conjugated version (see Figure 1). In addition, as described previously, the partially aromatized polymers are also more soluble and thus generally preferred.

5 Another advantage of EL polymers with electron withdrawing groups is their improved oxidative stabilities. Although undecyl PNV and unsubstituted PNV decomposed significantly after exposure to air and room lighting for one day, polymers with electron withdrawing groups showed no appreciable change. In fact, octyltrichloro PNV, di-*t*-butyl ester PPV, bistrifluoromethyl
10 PPV and trifluoromethylperfluorooctyl PPV were observed to still luminescence strongly after exposure to these conditions for one year. Quantitative measurements of di-*t*-butyl ester PPV showed that this material retained 70 percent of its original luminescence output after being exposed to intense ultraviolet radiation in air for one hour. In contrast, MEH-PPV and
15 aluminum trisquinolate, two commonly used emissive materials, decomposed almost entirely (with less than 5 percent of its original luminescence) under the same conditions.

EXAMPLE 9

As predicted by molecular calculations, the block polymers showed transfer
20 of excitons from the larger bandgap material to the smaller bandgap material. This effect is illustrated by Figure 2A which shows the emission spectra of bistrifluoromethyl PPV homopolymer, octyltrichloro PNV homopolymer, bistrifluoromethyl PPV/octyltrichloro PNV block copolymer and bistrifluoromethyl PPV/octyltrichloro PNV random copolymer when excited
25 at 345 nm. Figure 2B shows the emission spectra of octyltrichloro PNV homopolymer, bistrifluoromethyl PPV/octyltrichloro PNV block copolymer

and bistrifluoromethyl PPV/octyltrichloro PNV random copolymer when excited at 430 nm.

As shown by Figure 2A, when the block copolymer was irradiated at the excitation of the larger bandgap material, bistrifluoromethyl PPV, the emission peak characteristic of octyltrichloro PPV was more intense than that measured for octyltrichloro PNV homopolymer indicating that some excitons migrate to the block of octyltrichloro PNV before recombining. This spectrum also shows emission at wavelengths characteristic of bistrifluoromethyl PPV, indicating that some electrons and holes recombine before they reached the smaller bandgap block.

The spectrum of the random copolymer shows that its luminescence intensity is increased and that its luminescence maximum is slightly blue shifted relative to that of octyltrichloro PNV homopolymer. The luminescence wavelength maximum of the random copolymer more closely matches that of octyltrichloro PNV homopolymer since electrons and holes formed in larger bandgap segments where the concentration of bistrifluoromethyl PPV is higher, migrate to smaller bandgap segments where the concentration of octyltrichloro PNV homopolymer is higher. As with the block copolymer, the luminescence intensity of the smaller bandgap region is increased since excitons formed in large and small bandgap regions all recombine in the smaller bandgap regions. Emission measured at the wavelength of bistrifluoromethyl PPV is much less intense for the random copolymer than for the block copolymer showing that migration of electrons and holes into smaller bandgap segments of the random copolymer is more complete than for the block copolymer. This more complete migration most likely results from the fact that random copolymer contains units of both materials along the entire polymer chain. In other words, because the random copolymer

contains short blocks of the large bandgap and small bandgap materials compared with block copolymers, electrons and holes reach the smaller bandgap segment after traveling a much shorter distance.

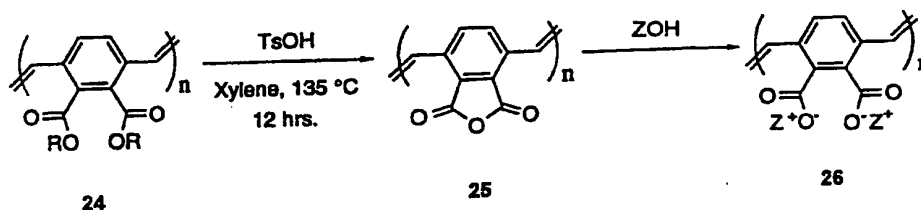
5 This interpretation is confirmed by Figure 2B. When irradiated at the excitation maximum of octyltrichloro PNV, the smaller bandgap homopolymer, the emission intensity of the random copolymer is greater than that of the block copolymer or the homopolymer. As with polymers containing conjugated and unconjugated segments, the increased emission intensity of the random copolymer is due to a reduction of non-radiative quenching of excitons. Quenching, which occurs at defects in the polymer backbone, is reduced in the random copolymer due to the presence of both large and small bandgap regions throughout the polymer backbone. Excitons become trapped in the smaller bandgap segments of the random copolymer and recombine with emission of light in these segments. The larger bandgap segments have been proposed to prevent migration out of the smaller bandgap regions and thereby diminish the number of electrons and holes that migrate to quenching sites. The emission intensity of the block copolymer is essentially the same as that of the homopolymer since only the octyltrichloro PNV block of the block copolymer is excited by 430 nm radiation. Because 10 excitons in the block copolymer are free to move throughout the entire length of the octyltrichloro PNV region, they are about as likely to reach quenching sites as in the homopolymer.

15 In films, the block copolymer shows luminescence characteristic only of the smaller bandgap homopolymer, octyltrichloro PNV. This more complete migration results from the increased interaction among the polymer chains in the solid state, which allows electrons and holes to be transferred between chains as well as along the polymer chain. The spectrum of a 1:1 mixture of 25

the two homopolymers does not show complete transport to the smaller bandgap polymer. The difference in these results is due to the fact that the mixture of homopolymers can more readily phase separate into macroscopic regions containing only one type of homopolymer. Migration of electrons and holes from the larger bandgap regions to smaller bandgap regions, thus would occur over larger distances than in films of the block copolymer.

EXAMPLE 10

A particularly interesting PPV was compound **24** (wherein R = *t*-butyl). As illustrated by Scheme 5, it may be converted to the water soluble dicarboxylate PPV **26**.



Conversion to the anhydride occurred rapidly in xylene at 135 °C in the presence of a small amount of acid catalyst. The bright orange-red anhydride **25** was identified by its two strong carbonyl stretches in the infrared spectrum at 1839 and 1763 cm⁻¹. This anhydride was converted to the dicarboxylate PPV **26** by mixing it with aqueous base. Because compound **26** is soluble in aqueous base, uniform, luminescent films of this polymer can be formed by spin casting the polymer from aqueous solution.

Thermogravimetric analysis of **24** under argon revealed that the same conversion to the anhydride occurs at 237 °C in the absence of acid catalyst. Further experiments showed that decomposition begins at 512 °C and continues until all of the polymer is gone at 700 °C. Anhydride **25** lost very

little mass until about 506 °C and then underwent the same course of decomposition that was observed for 24. Because polymer 24 is converted to polymer 27 at a lower temperature when acid is present, 24 can be used in conjunction with a photo-acid generator as a photoresist.

5 To test this application, polymer 24 containing about 50% unaromatized units was used to result in a highly soluble polymer. The polymer was blended with a photo-acid generator, triphenylsulfonium hexafluoroantimonate, by dissolving both materials in dichloromethane and then spin casting this
10 polymer solution onto a silicon wafer. The wafer was heated at 60 °C to drive off any remaining solvent and irradiated through a mask with deep ultraviolet radiation of 248 nm. During the irradiation step, triphenylsulfonium hexafluoroantimonate decomposed and generated hexafluoroantimonic acid. After irradiation, the wafer was heated at 150 °C to cause the polymer in the exposed acid containing areas to be converted to
15 anhydride 25. However, polymer 24 in the unexposed, acid free areas were not transformed at this temperature. The areas where polymer 24 was converted to anhydride 25 were then dissolved by immersing the wafer in an aqueous solution of the base tetramethylammonium hydroxide. The unconverted polymer regions, which are not soluble in aqueous base,
20 remained on the silicon substrate. As a result, polymer 24 when used in conjunction with a photo-acid generator, served as a positive photoresist.

EXPERIMENTAL METHODS

General Methods and Materials.

25 NMR spectra were recorded on a QE Plus-300 MHz (300.1 MHz ¹H; 75.33 MHz ¹³C) spectrometer. Infrared spectra were recorded using a Perkin-Elmer 1600 series FT-IR spectrometer. Elemental analyses were performed by Oneida Research Corporation or Mid-West Microlab. High resolution mass

spectra were obtained from UC Riverside Mass Spectrometry Facility. Ether was dried with sodium benzophenone. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). THF, hexane, benzene, and toluene were dried by passing through activated alumina columns. Grignard reagents, lithium reagents, alkylhalides, 3-bromo-4-fluoro-benzaldehyde, 1,4-dihalotetrafluorobenzenes, lithium diisopropylamide, and potassium *t*-butoxide were purchased from Aldrich and used without further purification. Tetrachlorobenzobarrelene was prepared as previously reported by Hales *et al.*, *Org. Synth.* **59**: 71 (1979), and chlorotrifluorobenzobarrelene was prepared by the synthesis described for bromotrifluorobenzobarrelene by Brewer *et al.*, *J. Chem. Soc. (C)*: 664 (1968), and purified by column chromatography (silica gel/hexane).

Acetylenes and protected diols were prepared according to literature procedures. Hexamethylphosphoramide ("HMPA") was purchased from Aldrich and dried over calcium hydride and then distilled under reduced pressure prior to use. 3,3,3-trifluoropropyne was purchased from PCR incorporated. *Cis*-3,5-cyclohexadiene-1,2-diol was obtained from ICI. Thiocarbonyldiimidazole ("TCDI"), 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine ("DPD"), 2,2-dimethoxypropane, perfluorooctyl iodide, pyridinium. *p*-toluenesulfonate ("PPTS"), methyl propiolate, 2-ethyl hexanol, acetylenedicarboxylic acid, hexafluoro-2-butyne, and SMI_2 in THF were purchased from Aldrich and used without further purification except where noted otherwise.

Gel permeation chromatography (GPC utilized an AM Gel Linear 10 column and a Knauer differential refractometer. Dichloromethane (Burdick and Jackson HPLC grade) was used as the eluent for all GPC measurements. Molecular weights are uncorrected and reported as compared to Shodex

polystyrene standards with molecular weights ranging from 2.95×10^3 to 2.40×10^6 . Benzene- d_6 was dried by passing through activated alumina columns. Dichloromethane- d_2 , tetrahydrofuran- d_8 , and hexafluoro-*t*-butanol ("HFB") were distilled from calcium hydride.

5 UV/Vis spectra were recorded on a HP Vectra ES/12 spectrometer. Thermogravimetric analyses were carried out using a TGA 7 Thermogravimetric Analyzer. Dichloromethane (Burdick and Jackson HPLC grade) was used as the eluent for GPC measurements. Emission spectra were recorded on an SLM 8000 C Spectrofluorometer. Xylene was purchased
10 from Aldrich in a Sure Seal container. Methanol, dichloromethane and chloroform were degassed by purging with dry argon for a minimum of 30 minutes. Hexafluoro-*t*-butanol (HFB) and THF- d_8 were distilled from calcium hydride.

6-Undecyl-1,4-dihydro-1,4-ethenonaphthalene
15 ("Undecylbenzobarrelene").

Method A: Under argon, decyl magnesium bromide (1.0 M ether solution, 100.8 mL) was added to a dry ether solution of 3-bromo-4-fluorobenzaldehyde (20.1 g, 0.099 mol, 0.99 M) at 0 °C over 20 min. After the addition was complete, the reaction mixture was stirred at 0 °C for an
20 additional 30 min and then at room temperature for 2 hours. An aqueous solution of HCl (1.82 M, 100 mL) was then added to quench the reaction at 0 °C, and a white precipitate was formed. The mixture was extracted with ether (3x 200 mL) and dried over Na_2SO_4 . After filtration and removal of the solvent, the resulting product was dissolved in benzene and dried under
25 vacuum. A yellow oil, 1-(3'-bromo-4'-fluorophenyl)-undecanol, was obtained in quantitative yield.

Under argon, a hexane (dry) solution of 1-(3'-bromo-4'-fluorophenyl)-undecanol (34.11 g, 0.099 mol, 0.40 M) was added, over 3.5 hours via an addition funnel, to a round bottom flask containing P_2O_5 (47 g, 0.33 mol) in refluxing hexane (dry, 250 mL). The resulting reaction mixture was refluxed for another 20 min. After filtration and removal of the solvent, 1H NMR spectroscopy showed the formation of 2-bromo-1-fluoro-4-(1'-undecenyl)benzene with < 5% impurity. The crude product was used for the next reaction without further purification.

A mixture of 2-bromo-1-fluoro-4-(1'-undecenyl)benzene (0.094 mol) and 10% Pd/C (398 mg) in ethyl acetate (200 mL) was stirred under a hydrogen balloon for > 12 hours and filtered through celite. The solvent was then removed under vacuum. The resulting orange oil was distilled between 141 °C/140 mtorr and 148 °C/130 mtorr to yield a colorless oil, 2-bromo-1-fluoro-4-undecylbenzene (95%). The isolated yield of 2-bromo-1-fluoro-4-undecylbenzene based upon 3-bromo-4-fluoro-benzaldehyde was 90%.

In a dry box, a THF (dry, 30 mL) solution of 2-bromo-1-fluoro-4-undecenylbenzene (12.6 g, 0.038 mol) and 1-bromo-2-chloroethane (5.75 g, 0.040 mol) was loaded into a 50 mL syringe. Using a syringe pump, this solution was added over 3 hours to a THF (dry, 50 mL) solution of 1,2-benzylidenedioxy-3,5-cyclohexadiene (3.79 g, 0.019 mol) and magnesium (4.5 g, 0.185 mol) at 60 °C (oil bath temperature). During the addition, gas was evolved. After the addition was complete, the reaction mixture was continuously heated at 60 °C for 12 hours. The solvent was then removed under vacuum. The resulting residue was loaded onto a plug of silica gel (175 mL) and eluted with 1200 mL of ether. After removal of ether, a yellow solid was obtained. The product was recrystallized by partially dissolving in warm pentane and cooling at -50 °C for 12 hours. Filtration of

the cold mixture afforded light yellow crystals of 6-undecyl-1,2,3,4-tetrahydro-2,3-(benzylidenedioxy)-1,4-ethenonaphthalene (4.91 g, 60% yield based upon 1,2-benzylidenedioxy-3,5-cyclohexadiene).

Under argon, a slurry of lithium diisopropyl amide (LDA, 7.70 g, 71.8 mmol) in diethyl ether (dry, 50 ml) was added to a mixture of 6-undecyl-1,2,3,4-tetrahydro-2,3-(benzylidenedioxy)-1,4-ethenonaphthalene (2.03 g, 4.68 mmol) and potassium *t*-butoxide (7.91 g, 70.5 mmol) in diethyl ether (dry, 50 mL at 60 °C (oil bath temperature) over 5 hours. After the addition was complete, the reaction mixture was kept at 60 °C for another hour. The resulting dark brown slurry was cooled with an ice bath, and water (4 mL) was added to quench the reaction. The mixture was then filtered through a plug of silica gel (100 mL) and eluted with 800 mL of ether. After removal of ether, the residue was loaded onto a silica gel column (7" x 2"), and eluted with hexane. The product was collected from 335 mL to 1300 mL. The solvent was removed to give a light yellow liquid, 6-undecyl-1,4-dihydro-1,4-ethenonaphthalene (1.18 g, 81.6%).

Method B: Undecyltrichlorobarrelene was converted to 6-undecyl-1,4-dihydro-1,4-ethenonaphthalene using the procedure previously reported for dechlorination of tetrachlorobenzobarrelene. A reaction starting with 0.5 g of undecyltrichlorobarrelene produced 97% yield of 6-undecyl-1,4-dihydro-1,4-ethenonaphthalene and a reaction starting with 15 g of undecyltrichlorobarrelene produced 80 % yield of 6-undecyl-1,4-dihydro-1,4-ethenonaphthalene following purification by column chromatography (silica gel/hexane). Both reactions were heated overnight. ¹H NMR (CDCl₃) δ 7.06 (d, J = 7.2 Hz, 1H), 7.02 (s, 1H), 6.88 (t, J = 3.6 Hz, 4H), 6.77 (d, J = 6.9 Hz, 1H), 4.89 (m, 2H), 2.51 (t, J = 7.8 Hz, 2H), 1.55 (p, J = 7.1 Hz, 2H), 1.27 (br, 16H), 0.89 (t, J = 6.6 Hz, 3H). ¹³C NMR (CDCl₃) δ 147.5, 144.8,

139.8, 139.5, 138.2, 122.9, 122.7, 121.7, 49.15, 48.74, 35.64, 31.91, 31.68, 29.67, 29.63, 29.59, 29.53, 29.48, 29.34, 22.69, 14.13. Exact mass (EI), m/e calcd for $C_{23}H_{32}$: 308.2504, obsd: 308.2505. Anal. calcd for $C_{23}H_{32}$: C, 89.54; H, 10.46. Found: C, 89.47; H, 10.43.

5 **6-octyl-5,7,8-trifluoro-1,2,3,4-tetrahydro-2,3-(benzylidenedioxy)-1,4-ethenonaphthalene ("Octyltrifluorobenzobarrelene").** 1-chloro-4-octyltetrafluorobenzene (1.1187 g) and *cis*-1,2-benzylidenedioxy-3,5-cyclohexadiene (0.5045 g) were each dissolved in 5 mL of ether in separate
10 flasks and then the two solutions were combined. After cooling this combined solution to 3 °C 2.53 mL of 1.57 M *n*-butyl lithium was added over 25 minutes. The reaction was stirred at 3 - 5 °C for an additional 20 minutes and then at room temperature for 1.5 hours. The flask was then cooled to 5 °C and 1.25 mL of 1.57M *n*-butyl lithium was added over 15
15 minutes. After stirring for 30 minutes at 5 °C the reaction was quenched by adding 2 mL of water. The total mixture was added into 30 mL of water and this was extracted with (4 x 100 mL) of ether. After drying over magnesium sulfate, the ether was evaporated to yield a viscous oil. The product could not be recrystallized, so it was purified by column chromatography. The silica gel column was eluted first with 5% ethyl acetate/hexane then 10%
20 ethyl acetate/hexane then 20% ethyl acetate/hexane. Product was obtained as 0.4483 g (40%) of a viscous yellow oil after removal of solvent. 1H NMR (300 MHz, $CDCl_3$) δ 7.50 (m, 2H), 7.38 (m, 2H), 6.61 (m, 2H), 5.80 (s, 1H), 4.67 (m, 2H), 4.33 (br s, 2H), 2.64 (t, J = 7.7 Hz, 2H), 1.56 (m, 2H), 1.27 (m, 12H), 0.88 (t, J = 6.5 Hz, 3H). ^{19}F NMR (470.56 MHz, $CDCl_3$,
25 referenced on $CFCl_3$ in benzene = 0.0 ppm) δ -129.60 (d, J = 18.8 Hz, 1 F), - 141.67 (d, J = 22 Hz, 1F), - 150.54 (t, J = 20.5 Hz, 1 F).

5-butyl-1,8-dihydro-1,8-etheno-3,4,6-trifluoronaphthalene by reaction of 1-chloro-4-butyltetrafluorobenzene with benzene. Under argon, 1-bromo-4-chloro-2,3,5,6-tetrafluorobenzene was dissolved in 83 mL of dry THF.

This solution was cooled to -78 °C in a dry ice/acetone bath and then 12.1
5 mL of 1.57 M butyl lithium in hexane was added over 15 min. After stirring this solution for 45 min, 20.5 g (0.190 mol) of butyl bromide was added over 10 min while maintaining the bath temperature at -78 °C. The solution was then slowly warmed to room temperature over 18 hours (temperature = -10 °C after 5 h). After removing the solvent and some of the excess butyl
10 bromide by rotary evaporator, followed by distillation at 64 °C to 70 °C, the remaining residue was dissolved in methylene chloride and extracted with a mixture of 10 mL of water and 4 mL of 1 M HCl. The organic layer was removed, and the aqueous layer was extracted with 3x35 mL of ether. All organic fractions were then combined and dried over magnesium sulfate. The
15 solvent was removed using a rotary evaporator, and the resulting residue was distilled under vacuum. 1-chloro-4-butyltetrafluorobenzene was collected as a colorless oil at 5 torr/56 °C. Yield = 4.023 g (88%).

Under argon, 0.5071 g of 1-chloro-4-butyltetrafluorobenzene was dissolved in 12.5 mL of ether. This solution was cooled to -78 °C in a dry ice/acetone
20 bath and then 1.4 mL of 1.57 M nBuLi in hexane was added over 15 min. The solution was stirred for 40 min during which time the bath temperature rose to -60 °C. Next, 83 mL of dry benzene was added over 1 hour while warming the solution to 10 °C. The solution was then stirred overnight and then heated at 35 °C for 2.5 hours. After this, 200 mg of ammonium
25 chloride was added. After evaporating the solvent, the remaining residue was added into 15 mL of water and 4 mL 1M HCl and then extracted with 5x30 mL of ether. The combined ether layers were dried with magnesium sulfate. Removing the ether yielded a yellow oil. ¹H NMR of this oil showed 43% 5-

butyl-1,8-dihydro-1,8-etheno-3,4,6-trifluoronaphthalene. The oil was distilled under vacuum and a few drops of 5-butyl-1,8-dihydro-1,8-etheno-3,4,6-trifluoronaphthalene were collected as a colorless oil at 86 °C/10 mtorr. The remainder of the oil formed a dark tar that looked like polymer by ¹H NMR. ¹H NMR (500 MHz, CDCl₃) δ 6.89 (m, 4H), 5.26 (m, A-B splitting, 2H), 2.57 (t, J = 7.6 Hz, 2H), 1.50 (pentad, J = 7.6 Hz, 2H), 1.33 (sextet, J = 7.5 Hz, 2H), 0.91 (t, J = 7.3 Hz, 3H). ¹⁹F NMR (470.56 MHz, CDCl₃, referenced on CFC1₃ in benzene = 0.0 ppm) d -153.69 (t, J = 20.5 Hz, 1F), -145.84 (d, J = 22.1 Hz, 1F), -133.46 (d, J = 17.9 Hz).

Alkyltrichlorobarrelene. Under argon, 14 g of tetrachlorobenzobarrelene was dissolved in 150 mL of dry THF and cooled to -78 °C. To this was added 31.5 mL of 1.6M n-BuLi over 20 minutes. The reaction, which turned dark purple, was stirred for 30 minutes. 10 equivalents of an alkyl iodide was added then to yield a cloudy mixture, or a solid with the higher melting iodides. The reaction was then removed from the dry ice acetone bath and allowed to warm to room temperature over several hours. After stirring overnight, THF was removed by rotary evaporator and the remaining solution was diluted with 100 mL CHCl₃. This solution was extracted with HCl (120 mL of 0.2 M HCl) and brine (2x100 mL). After removing solvent by rotary evaporator the excess iodide was removed by distillation. To prevent retro Diels-Alder reaction of the benzobarrelene, the heating bath temperature was kept below 100 °C. The remaining oil was further purified by column chromatography (silica/hexane) to yield a clear viscous liquid in 80 - 90% yield. Although the data presented is for undecyl substituted trichlorobarrelene, other alkyltrichlorobenzobarrelenes had nearly identical NMR spectra except for the alkyl region of the spectrum. ¹H NMR (CDCl₃): δ 6.91 (m, 4H), 5.43 (m, 2H), 2.83 (t, J = 9 Hz, 2H), 1.25 (bs, 18H), 0.88

(t, $J = 7.5$ Hz, 3H). Anal. Calcd for $C_{23}H_{29}Cl_3$: C, 67.08; H, 7.10 Found: C, 67.17; H, 7.04.

Alkyltrifluorobenzobarrelene. The method is analogous to that for alkyltrichlorobenzobarrelene described above except that
5 chlorotrifluorobenzobarrelene was used instead of tetrachlorobenzobarrelene. All alkyltrifluorobenzobarrelenes prepared had nearly identical NMR spectra except for the alkyl region of the spectrum. 1H NMR (500 MHz, $CDCl_3$): δ 6.89 (m, 4H), 5.27 (m, 2H), 2.56 (t, $J = 8$ Hz, 2H), 1.52 (m, 2H), 1.27 (br m, 12H), 0.88 (t, $J = 7$ Hz, 3H). ^{19}F NMR (500 MHz, $CDCl_3$): δ -133.5 (d, $J = 20$ Hz, 1F), -145.8 (d, $J = 24$ Hz, 1F), -153.7 (d, $J = 22$ Hz, 1F). Anal.
10 Calcd for $C_{20}H_{23}F_3$: C, 74.97; H, 7.24 Found: C, 74.85; H, 7.34.

Dimethylbarrelene-2,3-dicarboxylate ("Di-methylester barrelene"). Under air, a 50 mL round bottom flask ("RBF") was charged with 9 mL dimethylacetylenedicarboxylate (73.2 mmol) and 4.01 g (35.7 mmol) of *cis*-
15 3,5-cyclohexadiene-1,2-diol. The solution was heated at 60 °C for 1 day. Excess acetylene was removed under vacuum to yield a viscous yellow oil. The oil was loaded onto a column containing 1000 mL of silica gel, and eluted with 1000 mL 50% ethyl acetate/hexane followed by 1000 mL 80% ethyl acetate/hexane and 1000 mL 90% ethyl acetate/hexane to yield two
20 product isomers separately. Both isomers of dimethyl-2,3-dihydroxy-5,7-bicyclooctadiene-5,6-dicarboxylate were light yellow oils initially, but the anti isomer became a waxy solid upon standing. Total yield of both isomers was 95% (8.61 g, 33.9 mmol).

Dimethyl-2,3-dihydroxy-5,7-bicyclooctadiene-5,6-dicarboxylate (2.38 g, 9.35
25 mmol) and 1.94 g (90% pure, 9.80 mmol) of thiocarbonyldiimidazole ("TCDI") were loaded into a 50 mL flask, and purged with argon. 30 mL of

dry toluene was added to yield a yellow solution containing undissolved TCDI. The solution was heated in an oil bath that was preheated to 120 °C for 30 minutes. After cooling to room temperature, the solution was poured into 25 mL of 1 M HCl. The aqueous layer was extracted with 4 x 50 mL of
5 ether. The combined organic layers were then extracted with 2 x 5 mL 1 M HCl and 10 mL brine and then dried over magnesium sulfate. Evaporation of the solvent yielded 1.9 g of dimethyl-2,3-thiocarbonate-5,7-bicyclooctadiene-5,6-dicarboxylate as a yellow solid. Yield = 69%.

A 25 mL round bottom flask was charged with 1.85 g (6.24 mmol) of
10 dimethyl-2,3-thiocarbonate-5,7-bicyclooctadiene-5,6-dicarboxylate and 3.6 mL (97% pure, 18.0 mmol) of DPD to yield a brown mixture. The mixture was heated under argon in an oil bath at 40 °C for 5 days. The brown solution was then loaded onto a silica gel column and eluted with methylene chloride. After evaporation of solvent, 0.814 g (3.70 mmol) of dimethylbarrelene-2,3-
15 dicarboxylate was obtained as a pale yellow oil. Yield=61%. ¹H NMR(CDCl₃) δ 6.87 (m,4H), 5.11 (m,2H), 3.77 (s,6H). ¹³C NMR (CDCl₃) δ 165.79, 148.35, 139.39, 51.87, 49.00. FTIR 3075, 3003, 2954, 2845, 1714, 1648, 1602, 1580, 1435, 1331, 1313, 1270, 1236, 1192, 1118, 1056, 966, 939, 902, 885, 864, 844, 801, 751, 727.cm⁻¹ HRMS Calcd for C₁₂H₁₃O₄ (MH)⁺ 221.0811, found 221.0806. Anal. Calcd for C₁₂H₁₂O₄: C, 65.45;H,5.49 Found: C, 64.32; H, 5.72 (The sample contained ≈5% dimethylbenzene-1,2-dicarboxylate).
20

Di-*t*-butylbarrelene-2,3-dicarboxylate ("Di-*t*-butyl ester barrelene"). Acid impurities were removed from the di-*t*-butyl acetylene dicarboxylate by
25 loading it onto a plug of silica gel and eluting with 10% ethyl acetate/hexane. After removal of solvent, 3.8 g (16.8 mmol) of this purified material was put in a 50 mL RBF along with 0.924 g (8.24 mmol) of *cis*-3,5-cyclohexadiene-

1,2-diol. The flask was purged with argon and then 2 mL of dry THF was added. The reaction was heated for 10 days at 60 °C after which time ¹H NMR showed no diol starting material. Upon heating, the acetylene melted, and the diol dissolved. As the reaction progressed, the solution became cloudy and when the reaction was complete a significant amount of product had precipitated as a yellow solid. Once complete, the reaction mixture was dissolved in ethyl acetate and 25 g of silica gel was added. Solvent was evaporated to yield a free flowing solid which was then loaded onto a plug of 100 mL of silica gel and eluted with 50% ethyl acetate/hexane. Following removal of solvent, 2.12 g (6.302 mmol) of the pale yellow solid di-*t*-butyl-2,3-dihydroxy-5,7-bicyclooctadiene-5,6-dicarboxylate, was obtained as a mixture of two isomers. Yield = 75%. *Note:* To obtain a good yield, it is important that the temperature is not allowed to rise much above 60 °C. This reaction can also be done on a larger scale using 15 g of the diol starting material. Adding 3 equivalents of calcium carbonate relative to acetylene to this reaction was found to prevent the formation of phenol.

Di-*t*-butyl-2,3-dihydroxy-5,7-bicyclooctadiene-5,6-dicarboxylate (2.12 g, 6.30 mmol) and TCDI (1.31 g, 90 % pure, 6.62 mmol) were loaded into a 100 mL flask, and the flask was purged with argon. 20 mL of dry toluene was added to yield a yellow solution containing undissolved TCDI. The solution was heated in an oil bath that was preheated to 120 °C for 15 minutes. After cooling to room temperature, the yellow solution, which also contained a black precipitate, was poured onto a plug of 100 mL of silica gel and eluted with 50% ethyl acetate/hexane. Evaporation of the solvent yielded 2.15 g (5.65 mmol) of di-*t*-butyl-2,3-thiocarbonate-5,7-bicyclooctadiene-5,6-dicarboxylate as a light yellow solid.

A 100 mL RBF was charged with 13.57 g (35.66 mmol) of di-*t*-butyl-2,3-thiocarbonate-5,7-bicyclooctadiene-5,6-dicarboxylate and 21 mL of DPD to yield a brown mixture. The mixture was heated under argon in an oil bath at 40 °C for 1 week. The brown solution was then loaded onto a silica gel column and eluted with 10% ethyl acetate/hexane. After evaporation of solvent, the product was obtained as 6.7 g of a white crystalline solid containing ≈10% of the retro Diels-Alder benzene product. This mixture was dissolved in 200 mL of hot hexane and then cooled to -50 °C overnight. Solvent was decanted and the solid was washed with -50 °C pentane. Drying the solid under vacuum yielded the product as a colorless to white crystalline solid, and removal of solvent from the mother liquor yielded the benzene decomposition product as a clear colorless liquid. To remove any acid formed while heating, the solid was eluted through a plug of silica gel with 10% ethyl acetate hexane. Solvent was removed to yield 5.9 g (19.38 mmol) of the pure di-*t*-butylbarrelene-2,3-dicarboxylate as a white powder. Yield = 51%. ¹H NMR (CDCl₃) δ 6.84 (m, 4H), 5.02 (m, 2H), 1.49 (s, 18H) ¹³C NMR (CDCl₃) δ 164.84, 148.33, 139.65, 81.55, 49.57, 28.02. FTIR 2974, 2936, 1728, 1695, 1647, 1601, 1581, 1472, 1452, 1392, 1365, 1337, 1315, 1273, 1158, 1123, 1108, 1051, 1021, 937, 901, 880, 845, 765, 742 cm⁻¹. HRMS Calcd for C₁₈H₂₄O₄ 304.1669, found 304.1675. Anal. Calcd for C₁₈H₂₄O₄: C, 71.03; H, 7.95. Found: C, 71.22; H, 7.95.

2,3-Bis(2-ethylhexyl)bicyclo[2.2.2]octa-2,5,7-triene-2,3-dicarboxylate. A 100 mL round bottom flask was charged with 10.43 g (30.81 mmol) of 2-ethylhexyl acetylenedicarboxylate and 15.00 g (150 mmol) of CaCO₃. After stirring for 30 minutes under a flow of argon, 1.73 g (15.43 mmol) of *cis*-3,5-cyclohexadiene-1,2-diol and 2.13 mL of dry THF was added to the flask. The reaction was heated at 60 °C for 3 days and then filtered to remove CaCO₃. After rinsing the CaCO₃ with CHCl₃, solvent was removed under

vacuum to yield a yellow oil. The yellow oil was loaded onto a column of silica gel and eluted with 10% ethyl acetate/hexane. Following removal of solvent, 5.03 g (11.16 mmol, 71.20%) of a mixture of syn and anti product isomers of 5,6-bis(2-ethylhexyl)-2,3-dihydroxy-5,7-bicyclo[2.2.2]octa-5,7-diene-5,6-dicarboxylate was obtained as a yellow oil. *Note:* Calcium carbonate was added to this reaction to decrease formation of phenol.

5,6-bis(2-ethylhexyl)-2,3-dihydroxy-5,7-bicyclo[2.2.2]octa-5,7-diene-5,6-dicarboxylate (3.98 g, 8.84 mmol) and 1.93 g (90% pure, 9.72 mmol) of thiocarbonyldiimidazole (TCDI) were loaded into a 50 mL flask purged with argon. 30 mL of dry toluene was added to yield a solution containing undissolved TCDI. The solution was heated in an oil bath, which had been preheated to 135 °C, for 20 minutes. An additional 0.913 g of TCDI was loaded into the flask and the reaction was heated for 15 minutes. After cooling to room temperature, the yellow solution was poured onto a plug of silica gel and eluted with 50% ethyl acetate/hexane. Removal of solvent under vacuum yielded 4.01 g (8.15 mmol, 92.12%) of the 5,6-bis(2-ethylhexyl)-2,3-thiocarbonate-5,7-bicyclo[2.2.2]octa-5,7-diene-5,6-dicarboxylate as a yellow oil.

A 50 mL round bottom flask was charged with 4.013 g (8.15 mmol) of 5,6-bis(2-ethylhexyl)-2,3-thiocarbonate-5,7-bicyclo[2.2.2]octa-5,7-diene-5,6-dicarboxylate and 4.50 mL of DPD to yield a brown mixture. The mixture was heated under argon in an oil bath at 40 °C for 7 days. The brown solution was then loaded onto a silica gel column and eluted with 10% ethyl acetate/hexane. After evaporation of solvent, 1.78 g (4.27 mmol, 52.5%) of 2,3-bis(2-ethylhexyl)bicyclo[2.2.2]octa-2,5,7-triene-2,3-dicarboxylate was obtained as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 6.87 (m, 4H), 5.08 (m, 2H), 4.06 (dd, *J* = 6.0, 3.0 Hz, 4H), 1.59 (m, 2H), 1.39 - 1.28 (m, 16H),

0.88 (m, 12H); ^{13}C NMR (75 MHz, C_6D_6) δ 167.5, 149.7, 140.9, 68.2, 50.7, 39.5, 31.1, 29.6, 24.5, 23.7, 14.6, 11.5; HRMS calcd for $\text{C}_{26}\text{H}_{40}\text{O}_4 \text{M}^+$ 416.2926, found 416.2920. Anal. Calcd for $\text{C}_{26}\text{H}_{40}\text{O}_4$: C, 74.95; H, 9.68. Found: C, 74.87; H, 9.86.

5 **2,3-Bistrifluoromethylbicyclo[2.2.2]octa-2,5,7-triene ("Bis-trifluoromethylbarrelene")**. A Fischer-Porter bottle was charged with 9.16 g of *cis*-3,5-cyclohexadiene-1,2-diol (81.7 mmol) and purged with argon. 40 mL of dry THF was then added to yield a colorless solution. The flask was then closed and pressurized to 65 psi with hexafluoro-2-butyne. As the
10 pressure slowly decreased, more gas was admitted to maintain the initial pressure. After 1 week, the pressure was released and solvent was removed by rotary evaporator to yield 5,6-bistrifluoromethylbicyclo[2.2.2]octa-5,7-diene-2,3-diol as 21 g (76.6 mmol, 94%) of a white solid. The crude product, which appeared clean by ^1H NMR, was used in the next reaction
15 without further purification.

5,6-bistrifluoromethylbicyclo[2.2.2]octa-5,7-diene-2,3-diol (10.01 g, 36.5 mmol) and 7.53 g (90% pure, 38.0 mmol) of TCDI were put in a 500 mL round bottom flask and 150 mL of dry toluene was added. The flask was then put in an oil bath preheated to 130 °C. After 30 min, the reaction was
20 cooled to room temperature and poured into a separatory funnel containing 10 mL of 1M HCl. The aqueous layer was extracted with 3x100 mL ether. All organic layers were combined and dried over magnesium sulfate. After removal of solvent under vacuum, 5,6-bistrifluoromethylbicyclo[2.2.2]octa-5,7-diene-2,3-thiocarbonate was obtained as a brown solid. This was
25 dissolved in 100 mL of ethyl acetate and 50 g of silica gel was added. Following evaporation of the solvent under vacuum, the free flowing solid was loaded onto a column containing 750 g of silica gel and eluted with 20%

ethyl acetate/hexane and then 50% ethyl acetate/hexane. The product was obtained as two isomers (total = 9.91 g, 31.33 mmol, 86%). The major isomer, anti (identified by comparison to similar previously characterized compounds), was a white powder and the minor isomer, syn, was a slightly yellow crystalline solid.

A 450 ml, Schlenk flask was loaded with 4.336 g (13.7 mmol) of 5,6-bistrifluoromethylbicyclo[2.2.2]octa-5,7-diene-2,3-thiocarbonate and evacuated and then backfilled with argon three times. Next, 7.81 mL (97% pure, 41.1 mmol) of DPD, which was pumped down to 60 millitorr to remove volatile components, was added. This yielded a wet mixture, but most of the solid did not dissolve. The reaction was heated in an oil bath at 45 °C for 3 days. The flask was vented periodically to allow CO₂ formed by the reaction to escape. After cooling to room temperature, the product was vacuum transferred out of the reaction mixture into a Schlenk flask in liquid nitrogen. A second vacuum transfer yielded 2.078 g (8.65 mmol, 63%) of the desired product as a clear colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ 6.90 (m, 4 H), 5.092 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ 145.18 m, 139.85, 122.07 (q, J = 272.07 Hz), 47.92; ¹⁹F NMR (376 MHz, CDCl₃) δ -61.73 s; HRMS calcd for C₁₀H₆F₆ 240.0372, found 240.0381. Anal. Calcd for C₁₀H₆F₆: C, 50.02; H, 2.52; F, 47.47. Found: C, 49.89; H, 2.48; F, 47.21.

Perfluoro-2-undecyne. Under argon, 23.75 g (43.5 mmol) of perfluorooctyl iodide was loaded into a steel bomb and the bomb was then sealed and cooled to -78 °C. Approximately 4.8 g (51.0 mmol) of trifluoropropyne was condensed into the reaction vessel which was then sealed and warmed to room temperature; the pressure increased to 100 psi. The reaction was then heated for 24 hours at 210 °C. The pressure initially increased to ≈250 psi and then gradually decreased to <150 psi. After

allowing the reaction to cool to room temperature, the pressure was released and the product mixture was seen to be a reddish-purple liquid with some white precipitate. Distillation of two combined reactions at 86°C/14 torr yielded 43.79 g of product as a clear colorless liquid. ¹⁹F NMR revealed this liquid to be 96% pure with some perfluorooctyl iodide impurity.

Redistillation of this mixture at 94 °C/19 torr yielded 37.9 g (59.2 mmol, 65%) of pure 1-iodo-1-trifluoromethyl-2-perfluorooctylethylene.

Inside a nitrogen filled dry box, 17 g (88% pure, 267 mmol) of powdered KOH was loaded into a 250 mL round bottom flask. Outside the box, under argon, 38 g (59 mmol) of 1-iodo-1-trifluoromethyl-2-perfluorooctylethylene was added to the KOH to produce a slightly yellow slurry. A 15 cm Vigreux column and short path distillation condenser were placed on the flask and the pressure was reduced to 30 torr. The flask was put in an oil bath at 67 °C, and then the temperature of the bath was raised to 90 °C over 10 min. When the temperature reached 85 °C the reaction began to reflux and at 90 °C the reaction began refluxing vigorously and the distillation temperature was 76 °C. Redistillation of the mixture which collected in the receiver flask yielded 13.19 g (25.8 mmol, 44%) of the desired product and 8.3 g of recovered 1-iodo-1-trifluoromethyl-2-perfluorooctylethylene. ¹³C (100 MHz, neat w/C₆D₆ tube to lock) 121.82 (t J = 36.0 Hz), 118.96 (t J = 32.9 Hz), 116.11 (t J = 32.9 Hz), 114.45 - 106.00 m, 104.35 (t J = 33.3 Hz), 76.88 (q J = 56.7 Hz), 71.29 (t J = 38.5 Hz); ¹⁹F NMR (376 MHz neat w/C₆D₆ tube to lock) -55.66 (s, 3F), -83.05 (t J = 10.3 Hz, 3F), -103.72 (s, 2F), -122.44 (s, 2F), -123.16 (br s, 4F), -123.83 (s, 2F), -124.08 (s, 2F), -127.80 (s, 2F); HRMS calcd for C₁₁F₂₀ 511.9680, found 511.9667. Anal. Calcd for C₁₁F₂₀: C, 25.80; F, 74.20. Found: C, 24.95; F, 74.22. The high level of fluorine in this compound reportedly interfered with the carbon determination thus producing the low carbon value found. **Caution:** The

reaction can become extremely rapid and explode. Best results were obtained with the pressure reported. Using higher pressures to try to improve the reaction yield usually resulted in an explosion. Use necessary precautions.

5 **2-Perfluorooctyl-3-trifluoromethylbicyclo[2.2.2]octa-2,5,7-triene.** Under argon, 18.72 g (36.5 mmol) of perfluoro-2-undecyne and 5.56 g (34.9 mmol) of the *cis*-3,5-cyclohexadiene-1,2-dimethylacetal were loaded into a 100 mL round bottom flask, and 13 mL of dry THF were added to yield two clear liquid phases. The reaction vessel was sealed with a Kontes valve and heated
10 at 45 °C overnight. The reaction, which was now one clear colorless phase, was then cooled to room temperature, and solvent was removed to yield the product as a slightly cloudy liquid in quantitative yield. ¹H NMR showed clean 5-perfluorooctyl-6-trifluoromethyl-5,7-bicyclo[2.2.2]octa-5,7-diene-2,3-dimethylacetal with mainly one isomer. This crude material was used in the
15 next reaction without further purification.

5-perfluorooctyl-6-trifluoromethyl-5,7-bicyclo[2.2.2]octa-5,7-diene-2,3-dimethylacetal (1.29 g, 1.94 mmol) was dissolved in 30 mL of dioxane, and 30 mL of freshly prepared 6 M HCl was added to yield a slightly cloudy solution which separated into two clear phases when stirring was stopped.
20 After heating the reaction at 65 °C for 1 day in an open flask, the solution turned brown and about half of the solvent evaporated. ¹H NMR showed complete reaction and clean product. The reaction mixture was extracted with 4x100 mL of ether. Combined organic layers were extracted with 10 mL brine and 5 mL distilled water and then dried over sodium sulfate.
25 Residual water was removed by dissolving the mixture in chloroform and evaporating this by rotary evaporator. The crude material of 5-perfluorooctyl-6-trifluoromethylbicyclo[2.2.2]octa-5,7-diene-2,3-diol was used in the next reaction.

Alternatively, 5-perfluorooctyl-6-trifluoromethylbicyclo[2.2.2]octa-5,7-diene-2,3-diol was made by dissolving 5-perfluorooctyl-6-trifluoromethyl-5,7-bicyclo[2.2.2]octa-5,7-diene-2,3-dimethylacetal (1.29g, 1.94 mmol) in 9 mL of methanol and adding 97 mg of pyridinium *p*-toluenesulfonate to yield a clear colorless solution. The reaction was heated at 60 °C in an open flask. Methanol was added periodically to maintain the total volume around 9 mL. After 4 days, ¹H NMR showed complete reaction of the major isomer, but the minor isomer had not reacted much, so 11 mL of dioxane and 11 mL of 6M HCl was added. After heating 1 day at 60°C, the reaction was complete. The reaction was purified as described above to yield 1.1 g (1.78 mmol, 92%) of a brown oil. ¹H NMR (300 MHz, CDCl₃) δ 6.52 (m, 2H), 4.29 (br m, 1H), 4.22 (br m, 1H), 3.89 (s, 2H), 2.52 (br s, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -61.12 (m, 3F), -80.83 (t, 3F, *J* = 9.2 Hz), -108.67 (m, 2F), -120.26 (br s, 2F), -121.83 (br s, 6F), -122.76 (br s, 2F), -126.19 (br s, 2F). HRMS calcd for C₁₇H₆F₂₀O₂S 665.9687, found 665.9766. Anal. Calcd for C₁₇H₈F₂₀O₂: C, 32.71; H, 1.29; F, 60.87. Found: C, 32.60; H, 1.27; F, 60.85.

The procedure for preparing compound 5,6-bistrifluoromethylbicyclo[2.2.2]octa-5,7-diene-2,3-thiocarbonate was essentially the same as that described above for making 2,3-bistrifluoromethylbicyclo[2.2.2]octa-2,5,7-triene. Column chromatography was done on silica gel by eluting first with 10% ethyl acetate/hexane to obtain the major isomer and then 35% ethyl acetate/hexane to obtain the minor isomer. Both isomers of 5-perfluorooctyl-6-trifluoromethylbicyclo[2.2.2]octa-5,7-diene-2,3-thiocarbonate were white solids (82%).

The major, anti isomer of compound 5-perfluorooctyl-6-trifluoromethylbicyclo[2.2.2]octa-5,7-diene-2,3-thiocarbonate (3.3 g, 4.95

mmol) was put in a 25 mL round bottom flask and the flask was purged with argon. Addition of 3 mL (97% pure, 3.07 g, 15.8 mmol) of DPD only wetted the solid, none appeared to dissolve. The reaction was heated in an oil bath at 45 °C and after 1 day the reaction was a brown liquid. After three
5 days, the reaction mixture was loaded onto a plug of silica gel and eluted with 40% ethyl acetate/hexane. Removal of solvent yielded 1.9 g (3.22 mmol, 65%) of 2-perfluorooctyl-3-trifluoromethylbicyclo[2.2.2]octa-2,5,7-triene as a slightly yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 6.90 (m, 4H), 5.1415 (m, 1H), 5.1049 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -61.50 (m, 3F), -80.70 (t, *J* = 9.2 Hz, 3F), -108.61 (br d, 2F), -193.04 (br s, 2F), -
10 121.80 (br s, 6F), -122.67 (br s, 2F), -126.08 (br s, 2F); HRMS calcd for C₁₇H₆F₂₀ 590.0068, found 590.0170. Anal. Calcd for C₁₇H₆F₂₀: C, 34.60; H, 1.02; F, 64.38. Found: C, 34.40; H, 0.93; F, 64.24.

Bicyclo[2.2.2]octa-2,5,7-triene. A 250 mL round bottom flask was charged
15 with 8.22 g (45.6 mmol) of ethynyl *p*-toluenesulfonate and then purged with argon. Dry benzene (40 mL) was added to yield a colorless solution. In a separate flask, 6.94 g (45.6 mmol) of *cis*-3,5-cyclohexadiene-1,2-dimethylacetal was dissolved in 10 mL of dry benzene and this solution was then added to the first solution. The flask was sealed with a Kontes valve
20 and the reaction was heated to 80 °C and stirred for 14 hours. After this time, some white crystals had formed in the reaction mixture. The reaction was then cooled to room temperature and more crystals formed. Removal of solvent under vacuum yielded a white solid which was then recrystallized by dissolving it in hot acetone (250 mL) and then cooling the solution to -50 °C
25 overnight. The white crystals obtained were rinsed with -78 °C acetone and dried under vacuum to yield 13.38 g (40.3 mmol, 88%) of bicyclo[2.2.2]octa-5,7-diene-2,3-dimethylacetal-5-sulfonate. **Caution:** Ethynyl *p*-toluenesulfonate can contain acidic impurities which cause rapid exothermic

decomposition of *cis*-3,5-cyclohexadiene-1,2-dimethylacetal. This decomposition is especially violent if the two reactants are combined neat. Acid impurities were removed from ethynyl *p*-toluenesulfonate by eluting it through a plug of silica gel (20% ethyl acetate/hexane).

5 Bicyclo[2.2.2]octa-5,7-diene-2,3-dimethylacetal-5-sulfonate (10.68 g, 32.1 mmol) was put in a 2000 mL round bottom flask and the flask was evacuated and then backfilled with argon three times. The flask was then put in a bath at -20 °C and 1.6 L of SmI_2 solution (0.1 M in THF) was added while
10 maintaining the bath temperature at or below -20 °C. 90 mL of HMPA, which had been dried over calcium hydride and then distilled, was then added to the solution and the color changed from blue-green to dark purple. The reaction was stirred under argon for 90 minutes at a temperature of -20 °C and then 150 mL of a saturated solution of aqueous NH_4Cl was added. After stirring for one hour, over which time the solution was allowed to warm to
15 room temperature, THF was removed under vacuum. The remaining mixture was diluted with 50 mL of water and the aqueous layer was then extracted with (3x500) mL of ether. The combined organic layers were then extracted with (2x200) mL of brine and (2x200) mL 0.1 M NaOH. These aqueous layers were then extracted with (3x200) mL of ether. The combined organic
20 layers were dried over MgSO_4 and solvent was then removed under vacuum to yield a pink liquid. This was loaded onto a plug of silica gel and eluted first with hexane until all HMPA was eluted and then with 10% ethyl acetate/hexane. Removal of solvent yielded bicyclo[2.2.2]octa-5,7-diene-2,3-dimethylacetal as a light pink solid. Further purification was accomplished
25 using a silica gel column eluted with 10% ethyl acetate/hexane to yield the product as 4.2 g (23.6 mmol, 73%) of a white waxy solid.

In a 250 mL round bottom flask, bicyclo[2.2.2]octa-5,7-diene-2,3-dimethylacetal (3.75 g, 21.04 mmol) was dissolved in 80 mL of methanol and 1.09 g of pyridinium *p*-toluene sulfonate was added. The reaction, which was left open to the air, was heated at 70 °C and the methanol was replenished periodically as it boiled off. After 1 week, remaining methanol was removed under vacuum and the reaction was purified on a silica gel column eluted with 40% ethyl acetate/hexane. Removal of solvent under vacuum yielded 1.9 g (13.75 mmol, 66%) of bicyclo[2.2.2]octa-5,7-diene-2,3-diol as a white crystalline solid.

Under argon, 1.64 g (11.87 mmol) of bicyclo[2.2.2]octa-5,7-diene-2,3-diol was dissolved in 40 mL of dry toluene in a 250 mL round bottom flask and 2.5 g (90% pure, 12.62 mmol) of TCDI was added. The flask was put in an oil bath that had been preheated to 130 °C and the reaction was stirred for 10 minutes. 0.12 g (0.61 mmol) of TCDI was then added and the reaction was stirred for an additional 5 minutes at 130 °C. After removing solvent under vacuum, the solid was redissolved in ethyl acetate and 18 g of silica gel was added. Solvent was removed to produce a free flowing powder which was then loaded onto a column of 600 g of silica gel, and eluted with 40% ethyl acetate/hexane. Removal of solvent under vacuum yielded 1.73 g (9.60 mmol, 81%) of bicyclo[2.2.2]octa-5,7-diene-2,3-thiocarbonate as a white crystalline solid.

A 250 mL Schlenk flask was charged with 1.8 g (9.99 mmol) of bicyclo[2.2.2]octa-5,7-diene-2,3-thiocarbonate and was then evacuated and filled with argon three times. Under argon, 6 mL (97% pure, 6.13 g, 31.6 mmol) of DPD which had been pumped down to remove all volatile components was added to yield a mixture containing a lot of undissolved bicyclo[2.2.2]octa-5,7-diene-2,3-thiocarbonate. The flask was sealed and the

reaction mixture was heated at 40 °C for 5 days. The flask was vented periodically to allow CO₂ formed by the reaction to escape. The product, bicyclo[2.2.2]octa-2,5,7-triene, (0.70 g, 6.72 mmol, 67.3%) was then vacuum transferred out of the reaction mixture as a colorless liquid. ¹H (300 MHz, CDCl₃) δ 6.78 (m, 6H), 4.842 (m, 2H). ¹³C (75 MHz, CDCl₃) δ 140.60, 48.23. HRMS calcd for C₈H₈ 104.0624, found 104.0627. Anal. Calcd for C₈H₈: C, 92.26; H, 7.74. Found: C, 92.20; H, 7.74.

2-Octylbicyclo[2.2.2]octa-2,5,7-triene. 100 mg (0.342 mmol) of decynyl *p*-toluenesulfate and 52 mg (0.342 mmol) of *cis*-3,5-cyclohexadiene dimethyl acetal were heated neat under argon for 3 days. Flash chromatography on silica gel (10% ethyl acetate/hexane) yielded 6-octylbicyclo[2.2.2]octa-5,7-diene-2,3-dimethylacetal-5-sulfonate (106 mg, 0.24 mmol, 70%) as a colorless oil.

To 3.6 g (8.1 mmol) of 6-octylbicyclo[2.2.2]octa-5,7-diene-2,3-dimethylacetal-5-sulfonate dissolved in 4 mL of dry THF, was added under argon 420 mL SmI₂ solution (0.1 M in THF). The mixture was cooled to -20 °C and 26.5 mL HMPA was added to yield a dark purple solution. The reaction was kept at -20 °C for 1.5 h, treated with 42 mL saturated NH₄Cl solution and allowed to warm up to room temperature during which time the solution turned yellow and a white precipitate formed. The precipitate was filtered off and washed with diethyl ether several times, and then solvent was removed under vacuum. 20 mL brine was added to the remaining mixture and it was then extracted with diethyl ether. The ether was removed under reduced pressure and the product purified by passing through a plug of silica gel. HMPA was removed first by eluting with hexane and then the product was eluted using 10% ethyl acetate/hexane. Removal of solvent yielded 1.57

g (5.43 mmol, 67%) of 5-octylbicyclo[2.2.2]octa-5,7-diene-2,3-dimethylacetal as a colorless liquid.

5 5-octylbicyclo[2.2.2]octa-5,7-diene-2,3-dimethylacetal (1.57 g, 5.43 mmol) and pyridinium *p*-toluene sulfonate (0.3 g, 1.1 mmol) were dissolved in 100 mL of methanol and heated to 60 °C in an open flask for 3 days. Methanol was removed under reduced pressure and the product purified by flash column chromatography on silica gel (50% ethyl acetate/hexane). Removal of solvent under vacuum yielded 1 g of 5-octylbicyclo[2.2.2]octa-5,7-diene-2,3-diol (4 mmol, 74%) as a colorless liquid.

10 5-octylbicyclo[2.2.2]octa-5,7-diene-2,3-diol (1 g, 4 mmol) and TCDI (0.87 g, 4.4 mmol) were refluxed in 20 mL toluene for 30 min. The reaction mixture was eluted through a plug of silica with 30% ethyl acetate/hexane to afford 1.15 g (3.9 mmol, 98%) of 5-octylbicyclo[2.2.2]octa-5,7-diene-2,3-thiocarbonate as a white crystalline solid.

15 5-octylbicyclo[2.2.2]octa-5,7-diene-2,3-thiocarbonate (1.15 g, 3.9 mmol) was suspended in DPD (0.76 g, 11.7 mmol) and heated at 40°C under argon for 5 days. The reaction mixture was purified by flash column chromatography on silica gel (10% ethyl acetate/hexane) to yield 168 mg (0.78 mmol, 25%) of 2-octylbicyclo[2.2.2]octa-2,5,7-triene as a colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ 6.76 (m, 4H), 6.17 (dd, *J* = 6.1, 1.8 Hz, 1H), 4.68 (m, 1H), 4.49 (m, 1H), 2.06 (td, *J* = 7.1, 1.8 Hz, 2 H), 1.25 (br d, 12H), 0.88 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 155.4, 141.0, 139.9, 131.5, 52.5, 47.8, 33.7, 31.9, 29.5, 29.3, 29.1, 27.2, 22.7, 14.1; HRMS calcd for C₁₉H₃₀O₂ (M+H)⁺ 216.1877, found 216.1878.

20

Undecyl PNV. Reacted 68.5 mg of 6-undecyl-1,4-dihydro-1,4-ethenonaphthalene, 3.8 mg of Mo metathesis initiator, 7.8 μ L of HFB, in 0.6 g C_6D_6 for 40 minutes resulting in quantitative yield of the corresponding precursor polymer. GPC data (CH_2Cl_2): $M_n = 47700$, $M_w = 81000$, PDI = 1.70.

199.5 mg of this unaromatized polymer was reacted with 142.3 mg of DDQ in 20 mL methylene chloride for 3 hours at room temperature. 1 mL of NaCl-methanol solution was found to facilitate the precipitation of the polymer in methanol. After being dried under vacuum, aromatized undecyl PNV was obtained in 90% yield. 1H NMR ($CDCl_3$, all peaks were broad) δ 8.29, 8.02, 7.47, 2.82, 1.73, 1.23, 0.88; ^{13}C NMR ($CDCl_3$) δ 141.0 (m), 134.9 (m), 131.9 (m), 130.1 (m), 129 - 128.6 (m), 127.7 (m), 124.0 (m), 123.1 (m), 36.45 (br), 31.91, 31.70, 29.67, 29.36, 27.69, 14.13. UV/Vis (chloroform): $\lambda_{max} = 253, 444$ nm. Emission spectrum (chloroform, excited at 485 nm): $\lambda_{max} = 561$ nm. Φ (solution, $\lambda_{ex} = 485$ nm) = 0.5%. IR (KBr, pellet): 3038 (m), 2954 (s), 2926 (s), 2854 (s), 1622 (m), 1574 (m), 1510 (m), 1457 (s), 1377 (s), 956 (s), 821 (s) cm^{-1} .

Octyltrifluoro PNV. Reacted 70.1 mg of 5-octyl-1,8-dihydro-1,8-etheno-3,4,6-trifluoronaphthalene, 3.7 mg of Mo metathesis initiator, 7.8 μ L of HFB, in 0.6 g of C_6D_6 for 1.5 hours at room temperature resulting in a 99% yield of the corresponding precursor polymer. GPC CH_2Cl_2): $M_n = 28800$, $M_w = 36100$, PDI = 1.26.

64 mg of this unaromatized polymer was reacted with 41 mg of DDQ in 10 mL methylene chloride overnight at room temperature resulting in a 96% yield of octyltrifluoro PNV. During the course of reaction, 1H NMR ($CDCl_3$) showed broad peaks at δ 7.6-6.8, 1.54, 1.26, 0.85. FTIR (KBr,

pellet): 2956, 2925, 2854, 1648, 1570, 1458, 1387, 1276, 1203, 1123, 1049, 1035, 972, 891, 842, 594 cm^{-1} . UV/Vis (chloroform): $\lambda_{\text{max}} = 416 \text{ nm}$. Emission spectrum (chloroform, $\lambda_{\text{ex}} = 403 \text{ nm}$): $\lambda_{\text{max}} = 568 \text{ nm}$; (chloroform, $\lambda_{\text{ex}} = 485 \text{ nm}$): $\lambda_{\text{max}} = 579 \text{ nm}$; Φ (solution, $\lambda_{\text{ex}} = 403 \text{ nm}$) = 0.05%.

5 **Octyltrichloro PNV.** Reacted 84.4 mg of 5-octyl-1,8-dihydro-1,8-etheno-3,4,6-trifluoronaphthalene, 3.7 mg of Mo metathesis initiator, 7.8 μL of HFB, in 0.6 g of C_6D_6 overnight resulting in a quantitative yield of the corresponding precursor polymer. GPC data (CH_2Cl_2): $M_n = 15000$, $M_w = 16700$, $\text{PDI} = 1.11$.

10 21.2 mg of this unaromatized polymer was reacted with 12.3 mg of DDQ in 1.2 mL $\text{C}_6\text{D}_6\text{Br}$ or toluene- d_8 overnight at 120°C to yield 96% of octyltrichloro PNV. ^1H NMR (toluene- d_8): broad peaks were observed at δ 7.8-6.6, 1.8-0.8 with peaks at δ 1.3, 0.93. FTIR (KBr pellet): 3041, 2934, 2852, 1553, 1458, 1376, 1354, 1322, 1261, 1236, 1104, 980, 838, 788, 759, 721, 683, 667, 559 cm^{-1} . UV/Vis (chloroform): $\lambda_{\text{max}} = 437 \text{ nm}$. Emission
15 spectrum (chloroform, $\lambda_{\text{ex}} = 430 \text{ nm}$): $\lambda_{\text{max}} = 569 \text{ nm}$; (Film, $\lambda_{\text{ex}} = 430 \text{ nm}$): $\lambda_{\text{max}} = 570 \text{ nm}$; Φ (solution, $\lambda_{\text{ex}} = 430 \text{ nm}$) = 14%.

20 **Dimethylester PPV.** Reacted 0.423 g of dimethylbarrelene-2,3-dicarboxylate, 32.7 mg of Mo metathesis initiator (was added as a solution in 40 drops of C_6D_6), 66 μL of HFB, in 4.37 g C_6D_6 . The reaction mixture gradually became orange and then dark reddish-brown over the course of 30 minutes. After 1 week, ^1H NMR of the reaction showed that it was 89 % complete and that reaction had stopped. The yield of the corresponding precursor polymer was 85.5%. GPC data (CH_2Cl_2): $M_n = 16700$. M_w
25 24000, $\text{PDI} = 1.44$.

100 mg of this unaromatized polymer was reacted with 105.2 mg of DDQ in 16 mL dichloromethane at room temperature. During the course of the reaction, the mixture became cloudy yellow green and eventually cloudy orange. After purification, drying the polymer yielded a dark orange to red solid of dimethylester PPV. Yield = 92%. UV/Vis (chloroform): $\lambda_{\text{max}} = 400$ nm. Emission spectrum (chloroform, $\lambda_{\text{ex}} = 415$ nm): $\lambda_{\text{max}} = 479$ nm; Φ (solution, $\lambda_{\text{ex}} = 415$ nm) = 33%. FTIR 3024, 2950, 1725, 1636, 1478, 1438, 1263, 1220, 1152, 1111, 1063, 1008, 959, 834, 795, 752, 702 cm^{-1} . Note: Following a smaller scale reaction by NMR showed that all of precursor polymer is aromatized after 2 hours. Adding 0.5 mL of a saturated sodium chloride solution in methanol was found to facilitate much more rapid and complete precipitation of the polymer.

Di-*t*-butylester PPV. Reacted 0.501 g of di-*t*-butylbarrelene-2,3-dicarboxylate, 28.2 mg of Mo metathesis initiator (was added as a solution in 40 drops of benzene), 56 μL of HFB, in 3.8 g dry benzene. Over the course of 10 minutes, the reaction mixture changed color from yellow to light orange-brown. The mixture was stirred overnight and then quenched by adding 5 drops of degassed benzaldehyde. After purification and drying under vacuum, 0.385 g of the corresponding precursor polymer was obtained as a brittle light yellow solid. Yield = 77%. GPC data (CH_2Cl_2): $M_n = 19600$, $M_w = 23900$, $\text{PDI} = 1.22$. Note: Following a smaller scale reaction by NMR shows that all monomer is consumed after 2.5 hours. If any of the monomer has decomposed to form the acid however, reaction times will be considerably longer. 0.369 g of this unaromatized polymer was reacted with 0.281 g of DDQ in 28 mL dichloromethane overnight at room temperature. During the course of the reaction, the mixture gradually became cloudy yellow and somewhat luminescent under the room lighting. Following purification, the di-*t*-butylester PPV was dried under vacuum to yield 0.34 g

of a yellow-orange solid. Yield = 93%. For preparing polymer that was 80% aromatized, the procedure was identical except that 0.8 equivalents of DDQ were used. In this case, the polymer always dissolved completely in methylene chloride to yield a transparent yellow solution during purification.

5 ^1H NMR (CDCl_3) δ 7.66 (bs, 2H), 7.32 (bs, 2H), 1.62 (bs, 18H) ^{13}C NMR (CDCl_3) δ 167.05, 134.66, 133.13, 127.99, 126.74, 83.15, 28.21. UV/Vis (chloroform): $\lambda_{\text{max}} = 410$ nm. Emission spectrum (chloroform, $\lambda_{\text{ex}} = 422$ nm): $\lambda_{\text{max}} = 479$ nm; (film, $\lambda_{\text{ex}} = 480$ nm): $\lambda_{\text{max}} = 527$ nm; Φ (solution, $\lambda_{\text{ex}} = 422$ nm) = 72%. FTIR 2878, 2933, 1720, 1560, 1477, 1458, 1420, 1394, 1369, 1290, 1155, 1148, 1118, 957, 844, 824, 752, 696, 668 cm^{-1} . Anal.

10 Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_4$: C, 71.50; H, 7.33. Found: C, 69.49; H, 7.20. Note: Following a smaller scale reaction by NMR showed that all of the precursor polymer is aromatized after 2 hours. Adding 0.5 mL of a saturated sodium chloride solution in methanol was found to facilitate much more rapid and

15 complete precipitation of the polymer.

Polyphenylenevinylene anhydride. This reaction was best performed by using 100% aromatized di-*t*-butyl ester PPV that had not been dried. (*i.e.*, it was still wet with the methanol/methylene chloride mixture). For a typical reaction, 0.35 g (1.15 mmol) of wet di-*t*-butyl ester PPV was transferred into

20 a 250 mL round bottom flask with 80 mL of xylene (dry Aldrich Sure Seal). To this was added $\approx 40 - 50$ mg of tosyl acid, and the yellow mixture was stirred under argon and heated to 125°C . After the low boiling solvent boiled off, the reaction mixture quickly changed color from yellow to bright red. Heating was continued for 12 hours to ensure complete reaction and the

25 reaction mixture was then transferred to two 40 mL centrifuge tubes. After centrifuging, the light brown solvent was decanted from the bright red precipitate. The precipitate was then rinsed by shaking it with acetone and recentrifuging the mixture. After decanting the solvent, this process was

repeated 2-3 more times using acetone as the solvent. The dark red solid was then dried under vacuum to yield 0.197 g of a dark red brittle solid. Yield = 99%. This solid is only soluble in aqueous base, which opens the anhydride to yield the diacid, so it was identified by its infrared spectrum, which clearly shows the two carbonyl stretches expected of an anhydride. FTIR 3067, 3025, 2921, 1839, 1764, 1702, 1562, 1498, 1363, 1288, 1213, 1152, 974, 923, 893, 847, 798, 753, 696, 635, 603, 574 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_4\text{O}_3$: C, 69.78; H, 2.34. Found: C, 66.42; H, 2.74.

Polyphenylenevinylene sodium dicarboxylate. The sodium salt was prepared by dissolving polyphenylenevinylene anhydride in 0.2 N aqueous NaOH. Depending on the size of pieces of polyphenylenevinylene anhydride used, this reaction occurred nearly immediately, or it took a few hours of stirring, with the fastest reaction occurring when the polyphenylenevinylene anhydride was a fine powder. Upon reaction, the solution became the bright yellow luminescent color. Upon acidifying the solution with 1 M HCl, the polymer reprecipitated as an orange solid that was recollected by centrifuging the solution. FTIR of this solid showed it to be a mixture of the starting anhydride and the diacid. Precipitating the basic polymer solution by adding it into acetone, however, yielded a bright yellow solid. After drying under vacuum, FTIR of this material showed it to be the sodium salt, polyphenylenevinylene sodium dicarboxylate, with some water coordinated to it. NMR of polyphenylenevinylene sodium dicarboxylate was obtained by dissolving polyphenylenevinylene anhydride in 0.2 N NaOH in D_2O . ^1H NMR (D_2O) δ 7.50 (bs, 2H), 7.05 (bs, 2H) ^{13}C NMR (D_2O , CD_3OD was set at 49.00) δ 178.02, 138.39, 132.93, 128.20, 125.41. FTIR 3416 br (coordinated H_2O), 3031, 2922, 2850, 1578, 1451, 1384, 1229, 1030, 964, 881, 831, 804, 754, 697 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_4\text{O}_4\text{Na}_2 \cdot 3\text{H}_2\text{O}$: C, 41.68; H, 3.50. Found: C, 42.67; H, 3.54.

Bistrifluoromethyl PPV. Reacted 487.8 mg of 2,3-bistrifluoromethylbicyclo[2.2.2]octa-2,5,7-triene-2,3-dicarboxylate, 63.8 mg of Mo metathesis initiator, 129 μ L of HFB, in 0.6 g C_6H_6 for 3 hours. The polymer did not completely precipitate in methanol, so it was purified by eluting it through a plug of silica gel using methylene chloride. The dried recovered product (50% yield) was a white solid of the precursor polymer. GPC data (CH_2Cl_2): $M_n = 29600$, $M_w = 31700$, PDI = 1.07.

20.7 mg of the unaromatized polymer was reacted with 19.8 mg DDQ in 1.2 mL C_6D_6 Br overnight at 120°C. Yield = 95%. 1H NMR (C_6D_5 Br): broad peaks were observed at δ 7.6-6.6. FTIR (KBr pellet): 3049, 2968, 1475, 1421, 1383, 1300-1100, 1073, 1022, 971. 932, 872, 842, 764, 741, 695, 670, 659, 603, 563, 527, 480 cm^{-1} . UV/Vis (chloroform): λ_{max} 308 nm. Emission spectrum (chloroform. $\lambda_{ex} = 345$ nm): $\lambda_{max} = 449$ nm; (Film, $\lambda_{ex} = 345$ nm): $\lambda_{max} = 458$ nm; (Φ (solution, $\lambda_{ex} = 345$ nm) 20%.

Trifluoromethylperfluorooctyl PPV. Reacted 106.9 mg of 2,3-bis(2-ethylhexyl)bicyclo[2.2.2]octa-2,5,7-triene-2,3-dicarboxylate, 3.5 mg of Mo metathesis initiator, 7.8 μ L of HFB, in 0.9 g C_6F_6 /10 drops C_6D_6 overnight resulting in a 90% yield of the corresponding precursor polymer. 18 mg of this unaromatized polymer was reacted with 16 mg of DDQ in 1.2 mL C_6F_6 for 3 days at 120°C. This produced a polymer that contained <5% unaromatized units. Polymers containing more unaromatized units were obtained by using less DDQ or employing shorter reaction times. Yield = 89%. 1H NMR (C_6F_6/C_6D_6 , all peaks were broad): δ 8.02, 7.80, 7.48, 7.39. FTIR (KBr pellet): 1531, 1465, 1409, 1369, 1288, 1241, 1211, 1146, 1055, 978, 913, 851, 804, 746, 735, 725, 708, 668, 638, 562, 531 cm^{-1} . UV/Vis (C_6F_6): $\lambda_{max} = 328$ nm. Emission spectrum (C_6F_6 , $\lambda_{ex} = 356$ nm): $\lambda_{max} =$

443 nm; (Film, $\lambda_{\text{ex}} = 352$ nm): $\lambda_{\text{max}} = 465$ nm; Φ (solution, $\lambda_{\text{ex}} 356$ nm) = 65%.

5 **Doping of Undecyl PNV.** The red-orange thin films of polymer undecyl PNV were obtained by spin-coating their saturated chloroform solution on glass slides. In a dry box, when the thin films were immersed into a glass dish containing a solution of nitrosonium tetrafluoroborate ($\approx 300 - 400$ mg) in acetonitrile (30 mL), the red-orange films immediately turned dark green. After 10 seconds the films were removed from the dopant solution and rinsed with acetonitrile. The doped films were dried under vacuum. The thickness
10 of the films was ca. 500 - 2000 nm. Conductivity was measured with a standard four-point probe using a Princeton Applied Research (PAR) model 173 potentiostat, and a PAR model 175 universal programmer. Thickness of thin films was measured with a Sloan Dektak 3030 Profilingmeter. Conductivities were calculated using the equation:

$$\sigma = \frac{\ln 2}{\pi d} \cdot \frac{i}{V}$$

15 where σ is the conductivity, d is the film thickness, i is current, and V is potential.

20 **Undecyl-PNV/Octyltrifluoro-PNV Block Copolymer.** Reacted 68.5 mg of undecylbenzobarrelene, 3.9 mg of Mo metathesis initiator, 7.8 μL of HFB, 4 μL of THF in 0.6 g of C_6D_6 for 4.5 hours. Then added 73.1 mg of octyltrifluorobenzobarrelene dissolved in 10 drops of C_6D_6 and let the

reaction proceed for 3 days. The corresponding precursor was made in 91% yield. GPC (CH_2Cl_2): $M_n = 46400$, $M_w = 66000$, $\text{PDI} = 1.42$.

51.6 mg of this block copolymer precursor was reacted with 33.5 mg of DDQ in 10 mL of dichloromethane overnight at room temperature. Yield = 95%.

5 ^1H NMR (CDCl_3) shows broad peaks as for the two homopolymers. UV/Vis (chloroform): $\lambda_{\text{max}} = 439$ nm. Emission spectrum (chloroform, $\lambda_{\text{ex}} = 403$ nm): $\lambda_{\text{max}} = 568$ nm; (chloroform, $\lambda_{\text{ex}} = 485$ nm): $\lambda_{\text{max}} = 577$ nm; Φ (solution, $\lambda_{\text{ex}} = 485$ nm) = 0.5%.

10 **Undecyl-PNV/Octyltrichloro-PNV Block Copolymer.** Reacted 66.2 mg of undecylbenzobarrelene, 3.5 mg of Mo metathesis initiator, 6.9 μL of HFB, 3.6 μL of THF in 0.6 g of C_6D_6 for 3.5 hours. Then added 81.4 mg of octyltrichlorobenzobarrelene dissolved in 10 drops C_6D_6 and reacted for 3 days. Yield = 88%. 1st block $M_n = 35400$, $M_w = 61400$, $\text{PDI} = 1.73$; 2nd block $M_n = 47900$, $M_w = 67600$, $\text{PDI} = 1.41$. The precursor block copolymer was
15 then aromatized with DDQ to yield the undecyl-PNV/octyltrichloro-PNV block co-polymer.

Undecyl-PNV/di-*t*-butylester-PPV Block Copolymer. Reacted 67.7 mg of undecylbenzobarrelene, 3.7 mg of Mo metathesis initiator, 7.8 μL of HFB, 20 μL of THF in 0.5 g of C_6D_6 for 21 hours. Then added 67.2 mg of di-*t*-butyl ester barrelene dissolved in 10 drops of C_6D_6 and let the reaction proceed for
20 36 hours resulting in the corresponding polymer precursor in 95% yield. GPC (CH_2Cl_2): 1st block $M_n = 76900$, $M_w = 155800$, $\text{PDI} = 2.03$; 2nd block $M_n = 165800$, $M_w = 252100$, $\text{PDI} = 1.52$.

39.5 mg of this polymer precursor was reacted with 30.3 mg of DDQ in 8
25 mL of dichloromethane for 5 hours at room temperature. ^1H NMR shows

broad peaks characteristic of both homopolymers. Yield = 96% UV/Vis (chloroform): λ_{max} = 248, 398, 434 nm. Emission spectrum (chloroform, λ_{ex} = 420 nm): λ_{max} = 476 (peak), 504 (shoulder) nm; (Film, λ_{ex} = 449 nm): λ_{max} = 597 nm; (Film, λ_{ex} = 480 nm): λ_{max} = 592 nm; Φ (solution, λ_{ex} = 406 nm) = 25%. FTIR (film on NaCl, 90% aromatized): 2975, 2925, 2853, 1721, 1715, 1634, 1455, 1414, 1392, 1368, 1276, 1255, 1151, 1119, 959, 845, 824, 748 cm^{-1} .

Undecyl-PNV/di-*t*-butylester-PPV Random Copolymer. Reacted 67.1 mg of undecylbenzobarrelene, 66.2 mg of di-*t*-butyl ester barrelene, 3.6 mg of Mo metathesis initiator, 7.8 μL of HFB and 20 μL of THF in 0.5 g of C_6D_6 for 18 hours to yield 90% of the corresponding random polymer precursor. GPC (CH_2Cl_2 : M_n = 208800, M_w = 388900, PDI = 1.86.

41.5 mg of this polymer precursor was reacted with 28.6 mg of DDQ in 8 mL of dichloromethane for 5 hours at room temperature. ^1H NMR shows broad peaks characteristic of both homopolymers. Yield = 95% UV/Vis (chloroform): λ_{max} = 248, 428 nm. Emission spectrum (chloroform, λ_{ex} = 420 nm): λ_{max} = 528 nm; (Film, λ_{ex} = 406 nm): λ_{max} = 562 nm; (chloroform, λ_{ex} = 440 nm): λ_{max} = 529 nm; (Film, λ_{ex} = 480 nm): λ_{max} = 573 nm; Φ (solution, λ_{ex} = 426 nm) = 4.3%. FTIR (film on NaCl, 90% aromatized): 2977, 2925, 2854, 1722, 1715, 1634, 1621, 1470, 1455, 1416, 1392, 1368, 1286, 1256, 1150, 1118, 955, 846, 825, 757, 722, 668 cm^{-1} .

Octyltrifluoro-PNV/Bistrifluoromethyl-PPV Block Copolymer. Reacted 83.9 mg of octyltrifluorobenzobarrelene, 6.8 mg of Mo metathesis initiator, 15.6 μL of HFB, in 0.6 g of C_6D_6 for 5 hours. Then added 58.6 mg of bis-trifluoromethyl-barrelene dissolved in 10 drops C_6D_6 and reacted for 8 hours. The yield of the precursor block co-polymer was quantitative. GPC data

(CH₂Cl₂): 1st block Mn 8300, Mw = 9400, PDI = 1.14; 2nd block Mn = 15000, Mw = 17800, PDI = 1.18.

21 mg of this precursor block co-polymer was reacted with 15.3 mg of DDQ in 1.2 mL of C₆D₅Br overnight (at 120 °C). Yield = 93%. ¹H NMR (toluene-d₈): broad peaks were observed at δ 7.8-6.6, 1.8-0.8 with peaks at δ 1.3, 0.93. FTIR (KBr pellet): 3047, 2926, 2854, 1554, 1466, 1459, 1420, 1356, 1279, 1195, 1157, 1105, 981, 966, 931, 870, 939, 787, 759, 740, 696, 684, 668, 560 cm⁻¹. UV/Vis (chloroform): λ_{max} = 435 nm. Emission spectrum (chloroform, λ_{ex} = 430 nm): λ_{max} = 565 nm; (Film, λ_{ex} = 430 nm): λ_{max} = 570 nm; (chloroform, λ_{ex} = 345 nm): λ_{max} = 563 nm; (Film, λ_{ex} = 345 nm): λ_{max} = 567 nm; Φ (solution, λ_{ex} = 430 nm) = 15%.

Octyltrifluoro-PNV/Bistrifluoromethyl-PPV Random Copolymer.

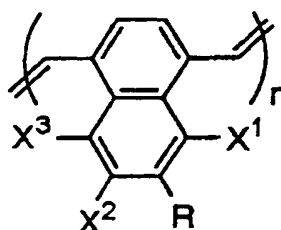
Reacted 51 mg of octyltrifluorobenzobarrelene, 33.5 mg of bis-trifluorobarrelene, 4.6 mg of Mo metathesis initiator, 9.3 μL of HFB, in 0.6 g of C₆D₆ for 10 hours resulting in quantitative yield of the corresponding polymer precursor. GPC data (CH₂Cl₂): Mn = 17000, Mw = 21900, PDI = 1.26.

21 mg of the polymer precursor was reacted with 15.2 mg of DDQ in 1.2 mL of C₆D₅Br overnight (at 120 °C). Yield = 94%. ¹H NMR (toluene-d₈): broad peaks were observed at δ 7.8-6.6, 1.8-0.8 with peaks at δ 1.3, 0.95. FTIR (KBr pellet): 3044, 2926, 2855, 1625, 1554, 1467, 1415, 1378, 1355, 1278, 1196, 1159, 1104, 981, 930, 840, 760, 742, 696, 669, 559 cm⁻¹. UV/Vis (chloroform): λ_{max} = 424 nm. Emission spectrum (chloroform, λ_{ex} = 430 nm): λ_{max} = 556 nm; (Film, λ_{ex} = 430 nm): λ_{max} = 562 nm; (chloroform, λ_{ex} = 345 nm): λ_{max} = 553 nm; (Film, λ_{ex} = 345 nm): λ_{max} = 561 nm; Φ (solution, λ_{ex} = 430 nm) = 26%.

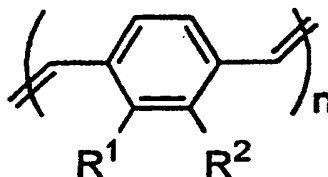
Although the present invention has been described with reference to preferred embodiments and selective Examples, it should be appreciated that these embodiments and Examples are for purposes of illustration only and are not intended to limit the scope of the appended claims.

What is claimed is:

1. An electroluminescent polymer comprising



or



wherein:

5

n is a positive integer;

X¹, X², X³, are each either hydrogen or an electron withdrawing group;

R, R¹ and R² are each hydrogen, halide, or a substituted or unsubstituted moiety selected from a group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, and aryl.

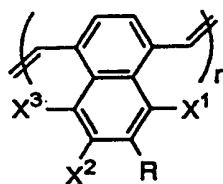
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2. The polymer as in claim 1 wherein the substituted moiety is functionalized with one or more functional groups selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine,

imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, peroxy, anhydride, carbamate, and halogen.

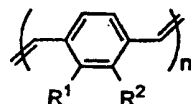
3. The polymer as in claim 1 wherein the moiety substitution is selected from the group consisting of C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl, C₂-C₁₀ alkynyl, and aryl, the moiety substitution optionally functionalized with one or more functional groups selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, peroxy, anhydride, carbamate, and halogen.

4. The polymer as in claim 3 wherein the polymer is a homopolymer.
5. The polymer as in claim 3 wherein the polymer is a block copolymer.
6. The polymer as in claim 3 wherein the polymer is a random copolymer.
7. The polymer as in claim 3 comprising



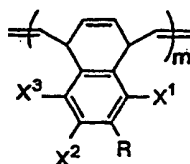
- wherein X¹, X², X³ are all the same and are selected from the group consisting of hydrogen and halide.

8. The polymer as in claim 7 wherein X^1 , X^2 , X^3 are selected from the group consisting of hydrogen, fluoride, and chloride and R is a C_1 - C_{20} alkyl.
9. The polymer as in claim 3 wherein R^1 and R^2 together forms a cyclic moiety.
- 5 10. The polymer as in claim 3 comprising



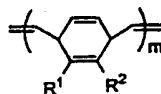
wherein R^1 and R^2 each is selected from the group consisting of hydrogen, C_1 - C_{20} perfluoroalkyl, C_1 - C_{20} carboxylic acid, C_1 - C_{20} carboxylate, C_1 - C_{20} ester, C_1 - C_{20} acid halide, C_2 - C_{20} acid anhydride, and C_1 - C_{20} amide.

- 10 11. The polymer as in claim 3 wherein R^1 and R^2 each is selected from the group consisting of hydrogen, C_1 - C_{10} perfluoroalkyls, and C_1 - C_{10} esters.
12. The polymer as in claim 7 further comprising



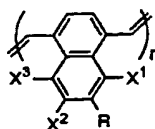
wherein m is a positive integer.

13. The polymer as in claim 10 further comprising



wherein m is a positive integer.

14. A method of making a polymer including repeating units of



wherein

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n is a positive integer;

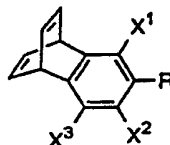
X¹, X², X³ are each either hydrogen or any electron withdrawing group;

R is hydrogen, halide, or a substituted or unsubstituted moiety selected from a group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, and aryl;

10

comprising:

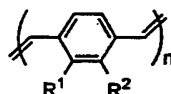
contacting a compound of the formula



with a metathesis catalyst to form a precursor polymer and aromatizing the precursor polymer.

15. The method as in claim 14 wherein the substituted moiety is functionalized with one or more functional groups selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, peroxo, anhydride, carbamate, and halogen.

16. A method of making a polymer including repeating units of



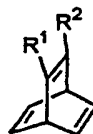
wherein

n is a positive integer;

R¹ and R² are each hydrogen, halide, or a substituted or unsubstituted moiety selected from a group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, and aryl;

comprising:

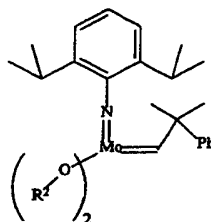
contacting a compound of the formula



with a metathesis catalyst to form a precursor polymer and aromatizing the precursor polymer.

17. The method as in claim 16 wherein the substituted moiety is functionalized with one or more functional groups selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, peroxo, anhydride, carbamate, and halogen.

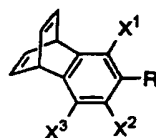
18. The method as in claim 14 or 16 wherein the metathesis catalyst is



wherein R^2 is $-C(CH_3)(CF_3)_2$.

19. The method as in claim 18 further comprising initializing the metathesis catalyst with an initiator.
20. The method as in claim 19 wherein the initiator is hexafluoro-*t*-butanol.
21. The method as in claim 19 further comprising modulating the activity of the metathesis catalyst with a Lewis base.
22. The method as in claim 21 wherein the Lewis base is tetrahydrofuran.
23. The method as in claim 14 or 16 wherein the aromatizing step is performed using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

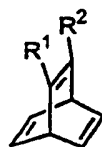
24. A method of making



wherein X^1 , X^2 , and X^3 are all the same and are halogen and R is a C_1 - C_{20} alkyl, comprising

reacting a halogenated benzene to form a benzyne;
 reacting the benzyne to form a halogenated benzobarrelene; and
 alkylating the benzobarrelene with RI.

25. A method of making



wherein R^1 and R^2 are each hydrogen, halide, or a substituted or unsubstituted moiety selected from a group consisting of C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, and aryl, the substituted or unsubstituted moiety optionally functionalized with one or more functional groups selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, peroxo, anhydride, carbamate, and halogen, comprising:

contacting cis-3,5-cyclohexadiene-1,2-diol or its acetonide protected form with $R^1C\equiv CR^2$ to form a bicyclo[2.2.2]octa-5,7-diene-2,3-diol;

converting the bicyclo[2.2.2]octa-5,7-diene-2,3-diol to a
bicyclo[2.2.2]octa-5,7-diene=2,3-thiocarbonate with thiocarbonyldiimidazole;
and

5 reacting the bicyclo[2.2.2]octa-5,7-diene-2,3-thiocarbonate with 1,3-
dimethyl-2-phenyl-1,3,2-diazaphospholidine.

26. A light emitting device comprising a polymer as described in claim 1.

27. A method for fabricating a light emitting layer comprising:
 dissolving a polymer as described in claim 1 in a solvent to produce a
polymeric solution and
10 spin coating the polymer solution onto a substrate.

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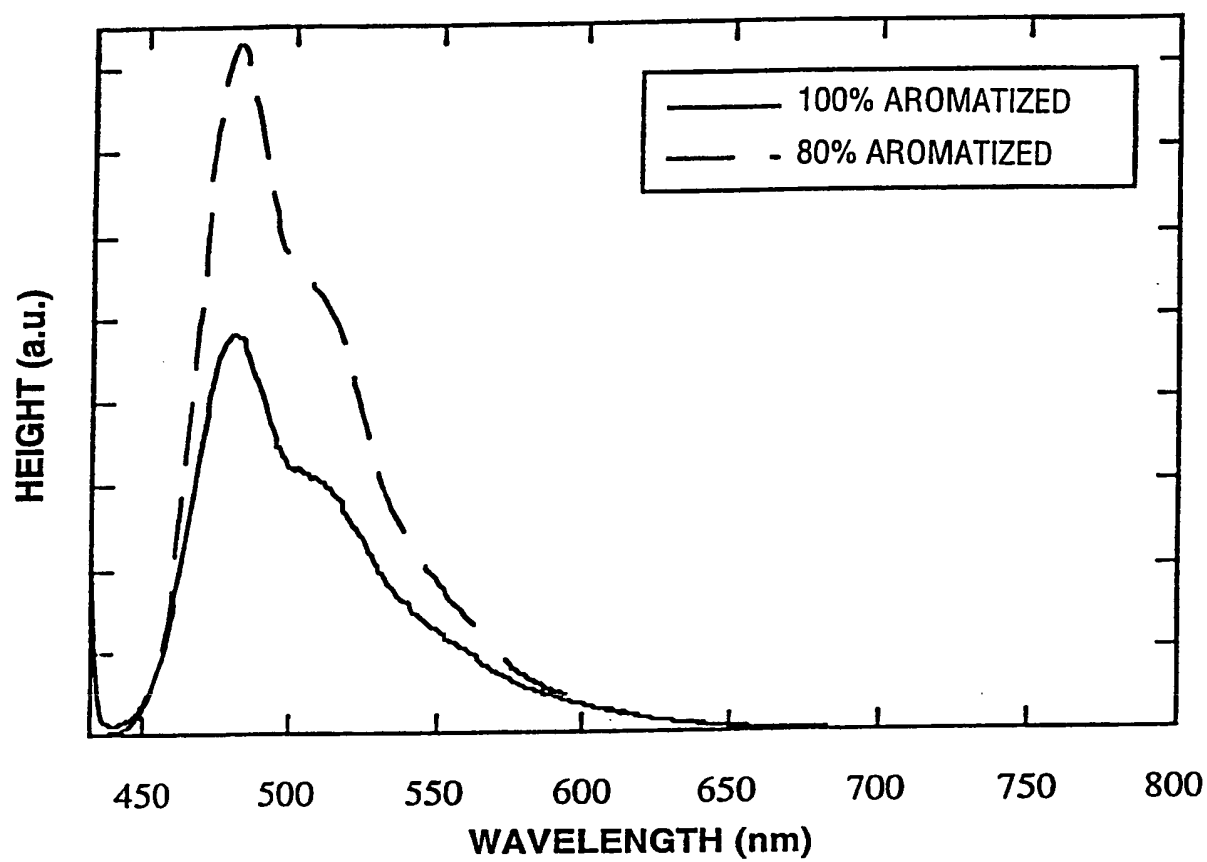


FIG. 1

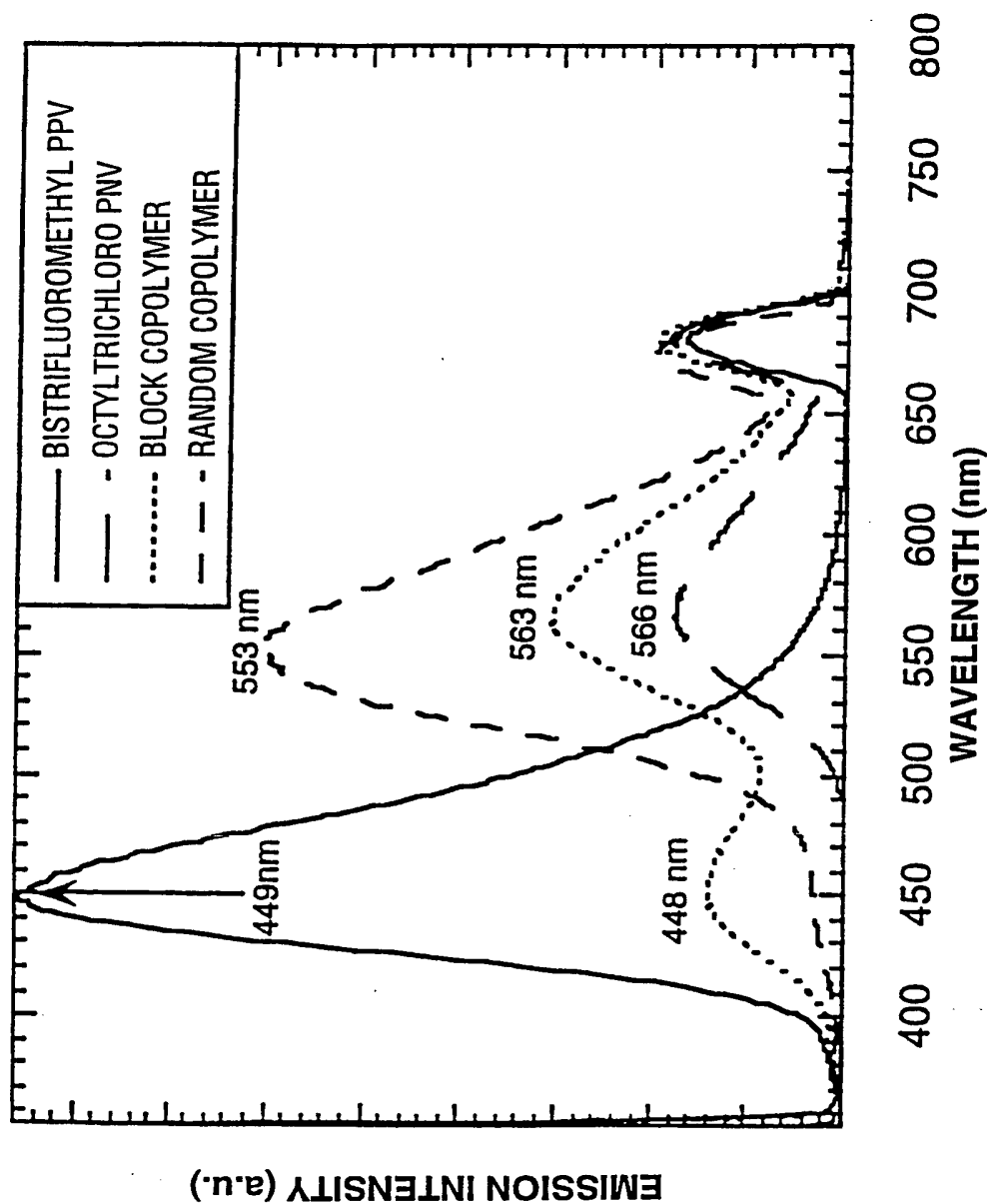


FIG. 2A

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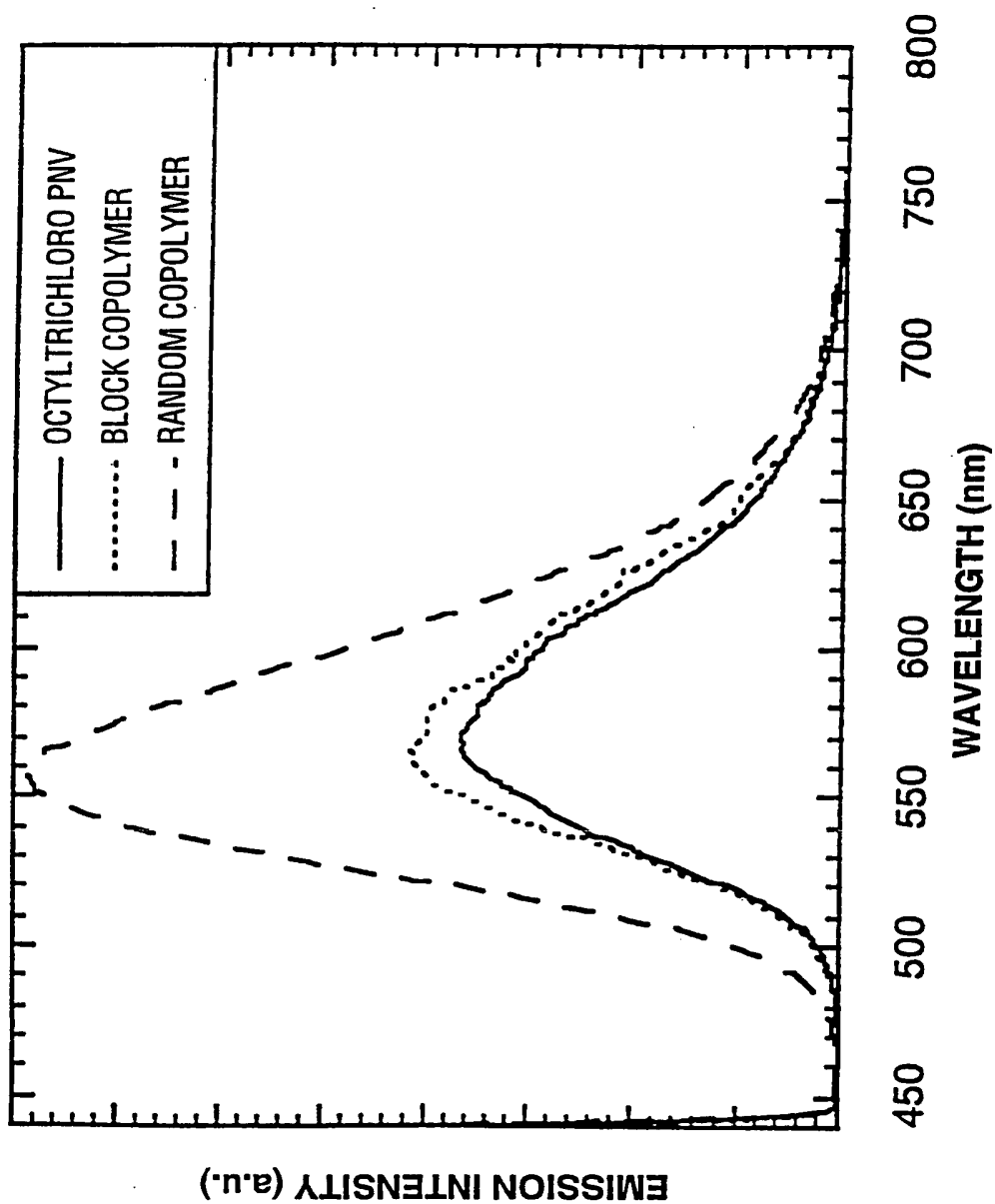


FIG. 2B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/07957

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08F 10/00; H01B 1/00

US CL : 526/280; 252/500

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 526/280; 252/500

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| Y | US 5,247,190 A (FRIEND et al.) 21 September 1993, columns 2-6. | 1-27 |
| Y,E | US 5,753,757 A (HSIEH) 19 MAY 1998, columns 5-10. | 1-27 |

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

| | | | |
|-----|---|-----|--|
| • | Special categories of cited documents: | "T" | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
| • A | document defining the general state of the art which is not considered to be of particular relevance | | |
| • B | earlier document published on or after the international filing date | "X" | document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone |
| • L | document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "Y" | document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| • O | document referring to an oral disclosure, use, exhibition or other means | | |
| • P | document published prior to the international filing date but later than the priority date claimed | "A" | document member of the same patent family |

Date of the actual completion of the international search

03 JULY 1998

Date of mailing of the international search report

20 JUL 1998

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